

CHAPTER 1

INTRODUCTION

1.1 Research Background

Energy is very important for living. Residential, household, transportation, agricultural, industrial and economic development activities all require energy. Energy resources can be divided into two categories:

- (a) Non-renewable energy (NRE) or fossil fuel that can be obtained from crude oil, natural gas and coal.
- (b) Renewable energy (RE) from biomass, wind, hydro power and solar energy.

Fossil fuels in the form of coal, crude oil and natural gas comprise 80% of the world's energy use (Suganthi and Samuel, 2012). With the rapid world population growth, increase in economic activities and the advent of globalization, the demand for energy consumption has increased exponentially. It is predicted that if the current global energy consumption pattern continues, the world energy consumption will increase by over 50% before 2030 (Oh et al., 2010). Figure 1.1 shows the trend of fossil fuels consumption worldwide and in the USA over the last few decades until year 2030 (Shafiee and Topal, 2008). Energy consumption is predicted to increase continuously on average by 2% per year for all three fossil fuels; oil, coal and natural gas. A yearly increase by 2% leads to a doubling of the energy consumption every 35 years. However, the energy generated from the combustion of fossil fuels is not feasible as the fuels are facing depletion and their price is estimated to increase in the future. Consumption of energy from fossil fuels also

creates environmental pollution such as the emission of greenhouse gases, hydrocarbons, nitrogen oxide and volatile organic compounds (Solangi et al., 2011)

Fig. 1.1: Consumption of fossil fuel worldwide and in the USA from 1949 to 2030 (Shafiee and Topal, 2008)

The major contributor to the greenhouse gas is the carbon dioxide emission which is increasing every year since 1982 (Ong et al., 2011). Therefore, renewable energy systems are favorable energy options in most industrialized countries, but the main challenge is to reduce their cost to a competitive level (Lund, 2009). Many industrial countries such as United States, Canada, Russia and Brazil started intensive research programs on renewable energy resources in the early 1970s. They have concentrated on solar energy installations for residential and commercial buildings. They have generated electricity from photovoltaic, wind, and ocean systems. Apart from that hydrogen fuel production from splitting of water and biomass has been used for conversion to heat, steam, and electricity (Klass, 2003).

In Malaysia the effort to materialize the use of renewable energy is rather slow. The government has intensified efforts to develop and promote the utilisation of renewable energy resources (Hashim and Ho, 2011). The Economic Planning Unit (EPU) of the Prime Minister's Office has been given the responsibility to plan and formulate policies for the development of renewable energy (RE) projects in Malaysia. Solar energy is being recognized as one of the promising technologies to replace conventional energy resources. This is due to the infinite and non-depletable energy from the sun. The amount of energy supplied by the sun to the earth is more than five orders of magnitude larger than the world's present electric power consumption (Hamakawa, 2002). Malaysia for example, has high solar energy potential with the daily average solar radiation of 4000–5000 Wh m⁻². The average sunshine duration was found to be in the range of 4–8 hours per day. Therefore, Malaysia has the favourable climatic conditions for the development of solar energy based applications (Mekhilef et al., 2012). The current solar energy applications in Malaysia can be divided into two main categories:

- (a) Solar thermal application: The heat from solar energy is harnessed for heating purposes.
- (b) Solar photovoltaic (PV) technologies: Arrays of cells which contain solar photovoltaic material convert the solar radiation into direct current electricity.

Although Becquerel discovered photovoltaic (PV) effect in 1839, the energy crisis of the 1970s is probably the greatest stimulant that intensified research and development (R&D) on solar cells. At present, over 80% of the world PV industry is based on crystalline-Silicon (c-Si) and polycrystalline-Silicon (pc-Si) wafer technologies (Razykov et al., 2011). However, these PV technologies are based on inorganic materials, which require high costs and highly energy consuming preparation methods. Another disadvantage of

silicon cells is the use of toxic chemicals in their manufacture. These aspects prompted the search for environmentally friendly and low cost solar cell alternatives.

Dye-sensitized solar cells (DSSCs) constitute an appealing alternative to the conventional silicon PV cells due to their relatively low production cost. The operation of the DSSC is inspired by the principle of natural photosynthesis. In 1991, dye sensitized nano-crystalline TiO₂ solar cells (DSSCs) based on the mechanism of a fast regenerative photoelectrochemical process was reported by Gratzel and co-workers. The overall efficiency of this new type of solar cell has now reached 12.3 % under simulated solar light (Yella et al., 2011).

The main difference between this type of solar cell and conventional PV cells is the use of a functional dye component. The dye which is responsible for light absorption is separated from the transport medium of charge carriers. Such a feature makes it possible for DSSCs to use low to medium purity materials prepared through low-cost processes, and to exhibit commercially realistic energy conversion efficiency. Furthermore, the materials used in DSSCs are environment friendly (Li et al., 2006). Efforts are continuously being undertaken to improve the performance of DSSCs and hence the competitiveness of this technology in the world market (Narayan, 2012).

1.2 Problem Statement

In this work, dye sensitized solar cells were fabricated using synthetic and natural dyes as light absorbers and PVDF-HFP based plasticized polymer electrolytes. Their performance were investigated. However, conventional PV solar cells have higher energy conversion efficiency compared to dye sensitized solar cells and this delays the commercialization of

DSSCs. There are still a lot of experiments and materials engineering that need to be carried out in order to enhance the efficiency and stability of DSSCs and to reduce their production cost. The preparation and characterization of suitable electrodes, dye materials and polymer electrolytes with optimum ionic conductivity and flexibility for application in DSSCs are the primary aims of this work. There is also the problem of electrolyte conductivity. For the improvement of polymer electrolyte conductivity, plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) will be added to the polymer-salt complexes. A conductivity of at least $10^{-4} \text{ S cm}^{-1}$ is to be achieved. According to Kang et al. (2007), the conductivity of $10^{-4} \text{ S cm}^{-1}$ is a threshold ionic conductivity. Below $10^{-4} \text{ S cm}^{-1}$ the ionic conductivity may play a key role in determining the photocurrent and the energy conversion efficiency of DSSC. Above the threshold ionic conductivity, the ionic conductivity may play a less-important role and other factors such as the recombination of the electrons on the surface of the TiO_2 layer with I_3^- in the electrolyte and the charge-transfer resistance at the interface between the counter electrode and the electrolyte may be critical. Once such threshold limit of ionic conductivity is obtained, it may be possible to determine and/or to eliminate problem(s) in the DSSCs fabricated.

1.3 Scope of The Reasearch

One of the primary aims of this study is to prepare plasticized PVDF-HFP based polymer electrolytes with optimum ionic conductivity and flexible properties that are suitable for the fabrication of dye sensitized solar cells. PVDF-HFP was chosen as the polymer host for the electrolytes because of its high dielectric constant of 8.4 (Choi et al., 2006) which can promote ion dissociation and thereby increase ionic conductivity in the polymer electrolyte. NaI and KI have been chosen as the main salts to provide the iodide ion conductivity in the electrolyte. NaI is the provider of Na^+ cations and I^- anions and KI is

the provider of K^+ cations and I^- anions. The reaction between the I^- anion and iodine will result in a triiodide ion to form the iodide/triiodide (I^-/I_3^-) redox couple for the DSSCs to work. In DSSCs, (I^-/I_3^-) redox couple becomes a mediator for electron transport in the electrolyte and for electron transfer at the electrode/electrolyte interface (Berginc et al., 2008). Salts with small cations are chosen since they have a large surface area to volume ratio for better adherence to the TiO_2 nanoparticles and dye molecules that allows changes in surface states of the semiconductor and dye molecules leading to changes in open-circuit voltage and short circuit current density. These changes can help to improve performance of DSSCs .

The fabrication of the dye sensitized solar cells also include the preparation and characterization of other components such as the dye material (synthetic Ruthenium 535 or N3 dye and anthocyanin and chlorophyll as natural dyes), photoelectrode and the counter electrode.

1.4 Objectives of The Present Work

Specifically, the main objectives of this thesis are to :

- (a) Develop a plasticized polymer electrolyte film with optimum ionic conductivity $\geq 10^{-4} S cm^{-1}$ at room temperature that is suitable for use in dye-sensitized solar cells.
- (b) Fabricate dye-sensitized solar cells (DSSCs) with highest possible efficiency using the polymer electrolytes developed with natural and synthetic dyes as the light absorbers.
- (c) Fabricate DSSCs using electrolytes with two iodide salts based on the electrolyte that gives the higher efficiency in (b) above in order to improve the efficiency further.

1.5 Thesis Organization

This thesis is divided into nine chapters. The current chapter (Chapter 1) introduces the research and gives a brief picture of the works undertaken. Chapter 2 is a review chapter that gives the state of the art research carried out worldwide on polymer electrolytes and DSSCs though the review is inexhaustive and far from complete. The chapter also provides the working principles of a dye-sensitized solar cell. The details of the experimental procedures and characterization methods used for preparing and optimizing relevant properties of the samples and devices are described in Chapter 3. The Chapters 4, 5 and 6 cover characterization results of the polymer electrolyte systems which are (PVDF-HFP)-KI, (PVDF-HFP)-KI-(EC/PC), (PVDF-HFP)-NaI and (PVDF-HFP)-NaI-(EC/PC). The results include FTIR, XRD and EIS studies. Chapter 7 presents results on the characterization of the DSSCs fabricated. The results obtained from the characterizations of polymer electrolytes and DSSCs are discussed in Chapter 8. The Chapter 9 concludes the thesis with some suggestions for further studies.