CHAPTER 1

INTRODUCTION

1.1 Background of Study

The elevation in global energy consumption is caused by the advancement of technology and the increase in the population. These factors have made the human population too dependent on fossil fuel, which is limited in resources, fluctuates in price, and has a severe environmental impact. The negative environmental impact should not be tolerated by reducing or eliminating reliance on fossil fuels. Furthermore, an effort must be done by improving the efficiency of the current process and focusing on the usage of renewable energy sources such as wind, hydro, biomass energy, geothermal, solar thermal, and hydrogen energy (Olabi, bahri, et al., 2021). Recently, the popularity of hydrogen energy has increased due to its higher energy content and lower environmental impact. The gravimetric density of hydrogen energy is seven times higher than the density of fossil fuels. As a result, it is one of the best alternative energies for the future, but there are a few issues that must be addressed such as transportation and storing hydrogen in designated materials arises (Kayfeci & Keçebaş, 2019; Tarhan & Çil, 2021).

Various methods have been developed to store hydrogen, especially via sorbents such as zeolites, metal organic frameworks (MOF), and carbon-based materials. Most of them have low densities and require additives for heat conductivity optimisation due to the limitation of the density levels of hydrogen to be stored, which need to be greater than 40 - 50 kg/m^3 and it is not easy to achieve that using available adsorbents except carbon-based materials. Carbon aerogel (CA) is an example of a carbon-based material that appears to have promising hydrogen storage properties due to its high specific area and porous structure (Yu et al., 2017). CA, in general, has unique properties such as superlight density, very high specific area, and electric conductivity, which make it a good candidate for composite reinforcement when compared to other aerogels. Aerogels can be synthesised usually by the sol-gel process. The chemical reaction parameter and processing steps need to be customised to control their composition and nano structuration. Then, a dry porous body of aerogels can be synthesised in monolithic form or granules. The microstructure of the aerogels is formed by a solid continuous network of primary and secondary colloidal particles connected to each other, either by condensation or crosslinking or by the formation and aggregation of fibrils due to the arrangement of polymer chains or macromolecules (Montes & Maleki, 2020).

Conventionally, CA can be synthesised by the carbonisation of organic aerogels such as cresol/formaldehyde aerogel. This method is expensive, uses a toxic carbon precursor, and involves a complicated synthesis process. Thus, it becomes less suitable for mass production and commercialisation due to safety concerns. Several research have been performed on cellulose-based CA because cellulose is renewable, biocompatible, non-toxic, and biodegradable. They used cellulose as their carbon precursor to synthesis CA. For instance, Yang et al. (2021) prepared CA using cellulose extracted from luffa sponge, and Wang et al. (2018a) prepared CA from cellulose aerogel (Yang et al., 2021; Yu et al., 2018a).

Sodium carboxymethyl cellulose (CMC) is a type of cellulose derivative formed by carboxymethylation of the hydroxyl group in cellulose molecules. CMC can be crosslinked with metal ions such as nickel (Ni^{2+}), calcium (Ca^{2+}) and magnesium (Mg^{2+}) to enhance its properties due to the presence of the carboxyl group.

Yu et al. (2017) synthesised enhanced CA-Ni from CMC-Ni aerogel as a result of the crosslinking reaction between Ni^{2+} and CMC via the sol-gel process. They succeed in preparing enhanced CA-Ni with a high specific capacity that exhibits excellent stability as energy storage (Yu et al., 2017). Other than that, Yu et al. (2018a) used ferric trichloride ($FeCl_3$) and collagen as crosslinking agent and nitrogen source respectively, in preparation of nitrogen-doped CA from CMC via a multistep approach such as sol-gel, freeze-drying, carbonisation and KOH activation processes. The obtained CA exhibited a well-developed porous structure and a high specific surface area for energy storage purposes (Yu et al., 2018a). This demonstrated the importance of metal ions in improving the structure of CA derived from CMC.

In this research, a direct, simple, and low-cost approach for synthesising CA composites through the carbonisation of sodium CMC aerogels via sol-gel and freeze-drying processes was investigated. Several metal ions were used as a crosslinking agent, including magnesium ions (Mg^{2+}), manganese ions (Mn^{2+}), nickel ions (Ni^{2+}) and zinc ions (Zn^{2+}). The CA-Mg composites had shown a high surface area and a porous structure. When analysed as hydrogen storage materials, the CA-Mg composites have the most efficient way of desorbing hydrogen compared to pure CA. The current research demonstrates a direct, simple, and low-cost method to synthesis CA-Mg composites as hydrogen storage materials.

1.2 Problem Statement

Conventionally, CA is made up from carbonisation of organic aerogels such as cresol/formaldehyde aerogels and phenol/formaldehyde aerogels. However, the disadvantages in using these methods are expensive, utilised toxic carbon sources, and involve complicated synthesis process which make them less suitable for mass production and commercialisation due to safety concerns (Alizadeh Asl et al., 2017; Aravamudhan et al., 2014; Ergun et al., 2016; Yu et al., 2017).

Recently, various research has been performed utilising cellulose sources due to its renewability and biocompatibility. Researchers choose cellulose as their research subject due to it being plenteous in nature that make it renewable, sustainable, and environmentally friendly. In preparing CA, CMC can be used as a starting precursor which needs to go through several processes, starting with gelation, followed by solvent exchange, freeze drying and finally pyrolysis. All steps involved are simple and can be deemed to be a green technique (Li et al., 2020; Peydayesh et al., 2022). CMC is a nontoxic, biocompatible, and water-soluble cellulose molecule. Owing to the present of carboxyl groups, CMC can be cross-linked with metal ions to enhance its properties. Due to the promising potential of CA in energy storage applications, substantial work involving the fabrication of CA cross-linked with metal ions has been conducted, such as the derivation of CA/NiO composites and the preparation of sodium polyacrylate functionalised carbon nanotube aerogels (Fest et al., 2023).

Carbon based materials are the most suitable materials for gas storage due to their very small pores, high porosity, and the attractive force between carbon atoms and gas molecules (Kayfeci & Keçebaş, 2019). The features of CA, such as its high porosity, make it ideal for hydrogen energy storage. Absorption process is involved to store hydrogen via physical bonding of van der Waals forces between materials with a high surface area and molecular hydrogen (Pandey et al., 2020). Different adsorbents can be used to store hydrogen, such as carbon-based materials, zeolites, and metal-organic frameworks (MOF) but most of them have low densities and require additives for heat conductivity optimisation due to the limitation to the density levels of hydrogen to be stored, which needs to be greater than 40-50 kg/m^3 and it is not easy to achieve that using available adsorbents (Olabi, Bahri, et al., 2021).

Previous research shows that, the standard set by Department of Energy (DOE), United State where the storage must be at least 6 wt% for application in the transportation industries, could not be achieved. The current research on carbon-based materials shows the value of 5.5 wt% hydrogen uptake at room temperature, which can be considered the best to meet DOE’s standard (Singh et al., 2020). Hence,research on carbon-based materials needs to be explored and varied to achieve DOE’s goal.

In this research, CA-Mg composites are synthesised by direct pyrolysis of CMC aerogels. CMC aerogels are prepared beforehand through the sol-gel process and freeze-drying with the addition of Mg^{2+} as a cross-linking agent. The synthesised CA-Mg composites have a high surface area and a porous structure, which can be suggested as a potential solution for hydrogen storage materials (Millet, 2014; Pyle et al., 2016; Zhao et al., 2021).

1.3 Objective of Research

The aim of the study is to investigate the potential of CA as hydrogen storage device for future applications, with the following objectives:

a) To synthesis CA from CMC via gelation process, freeze-drying, and pyrolysis.

b) To characterise CA derived from CMC using Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) method and Field Emission Scanning Electron Microscopy

(FESEM).

c) To investigate the ability of CA as an absorbent for hydrogen storage application using Temperature Programmed Desorption (TPD) technique.

1.4 Scope of Study

The main purpose of this research is to study the capability of CA as a hydrogen storage material from CMC. The synthesis of CA from CMC involved several steps, such as the gelation process, freeze-drying, and pyrolysis. CMC was treated with four metal ions during the sol-gel/gelation process: magnesium ion (Mg^{2+}), manganese ion (Mn^{2+}), nickel ion (Ni^{2+}), and zinc ion (Zn^{2+}), which acted as cross-linking agents to form hydrogel solution. Then, it was converted into CMC aerogel by a freeze-drying process followed by a pyrolysis process to form CA. The characterisation of CA was carried out using FTIR spectroscopy, XRD, BET method and FESEM. The prepared CA's ability to store hydrogen was investigated using the TPD technique.