CHAPTER 1

INTRODUCTION

1.1 HYDROGEN ECONOMY

The extensive consumption of fossil fuels over the past century has led to serious concerns like global warming, ozone layer depletion and acid rain. A long term energy supply solution that is practical, low cost, and clean is required. Renewable energy sources such as solar, wind currently cannot be used directly as fuel and require a storage medium because of their intermittent nature. Among the many choices, hydrogen has been identified as a potential energy carrier that can be stored, transported and distributed. Hydrogen is the most abundant element on earth and is considered as a leading candidate as energy carrier. However, elemental hydrogen is not available in substantial quantity on earth and is found in combination with carbon in hydrocarbons and with oxygen in water. Hydrogen is not a source of energy, but only a carrier of energy and requires technology to be produced (Barbir 2005a).

Hydrogen generated on-site using a variety of technologies could lead to development of decentralized micro power plants and vehicles based on hydrogen (fuel cells, internal combustion engine utilizing hydrogen) would dramatically reduce emissions of particulates, carbon monoxide, sulphur and nitrogen oxides and other local pollutants as the only by product of combustion is water (Dunn 2002). A well established method of deriving hydrogen is electrolysis, which involves the use of electricity to split water
into hydrogen and oxygen atoms. At present, roughly 4% of the world’s hydrogen is derived from the electrolysis of water (Committee on . This process produces extremely pure hydrogen in small amounts. However, electrolysis remains expensive at larger scales, primarily because of the electricity, which currently costs on an average three to five times as much as a fossil fuel feedstock. While water electrolysis is the most expensive process of producing hydrogen today, cost decline are expected over the course of the next decade as the technology improves. The U.S Department of Energy’s (DOE) Hydrogen Program FY 2005 had an objective to increase the production of hydrogen to 1500 kg/day for hydrogen refuelling stations using a low cost, high pressure water electrolyzer system for hydrogen production. Hydrogen produced on site and on demand using electrolyzers reduces the costs of transportation and storage making it competitive with delivered hydrogen. Electrolysis from renewable energy would result in a very clean hydrogen cycle. “Life cycle” comparisons of the hydrogen production process suggest that electrolysis from renewable energy holds environmental advantages over natural gas reformation, an energy system based on hydrogen from renewable resources, if accomplished on a large scale, could improve energy security, air quality, and greenhouse gas management. Such a system will require development across a series of technologies for hydrogen production, transportation, storage and use.

1.2 HYDROGEN PROPERTIES

Hydrogen is an attractive energy carrier due to its high energy/weight ratio. The energy density of hydrogen is 122 kJ/g and is about three times higher than that of hydrocarbon fuels. The energy per unit volume is 0.013 J/m. Its density is 0.084 g/L at normal temperature and pressure. The lower density makes the fuel safer because it increases the buoyancy force for speedy diffusion of the fuel in case of a leak.
1.3 HYDROGEN ENERGY

In recent years, the increased demand for high efficiency energy supplies have led to active research on alternative approaches for energy production that are environmentally friendly and low cost. Clean energy is considered as the solution to world’s increasing energy demand due to concerns regarding pollution and contamination (Rifkin 2002). Hydrogen as an attractive fuel for power generation and transportation is increasingly being addressed to overcome issues associated with fossil fuels. Hydrogen is considered as clean fuel and when used in fuel cells it produces only clean water besides electricity. Hydrogen can be produced by steam reforming of hydrocarbon fuel or by electrolysis of water. Methods such as high temperature steam electrolysis, thermolysis is also known. Out of these methods, water electrolysis produces clean hydrogen without any elaborate cleaning systems that are required when hydrogen is produced by steam reformation of fossil fuels. The process of producing hydrogen by electrolysis proceeds with high efficiency (Millet et al 2009). The energy required for production of hydrogen by electrolytic method is very high (4.5-5 kWh/Nm$^3$ of H$_2$) in most industrial electrolyzer. The process of formation of hydrogen and utilization of hydrogen to produce energy is called hydrogen energy system.

1.4 HYDROGEN FUTURE
hydrogen production by other techniques and improving the existing technologies is important

1.5 PRODUCTION OF HYDROGEN

The development of renewable, efficient and economical hydrogen production technologies is a key step towards a sustainable “Hydrogen energy resource” (Balat & Kirtay 2010). Electrolysis from renewable energy would result in a very clean hydrogen cycle. It also represents a potentially enormous source of hydrogen and could meet the projected demand even though the cost of delivering the energy would be higher initially than that produced from fossil fuel/natural gas (Romm 2004). With the improvements in technology and mass production the cost is likely to reduce.

Electrolysis of water is one of the major methods of producing clean hydrogen; this electrolysis may be carried out using aqueous alkaline electrolytes or with solid polymer electrolytes.

1.6 RESEARCH MOTIVATION

In the light of the importance of the development of clean energy technology and hydrogen energy systems many national/international research groups are involved in addressing many issues towards development of materials (catalysts, membranes and electrodes), systems (electrolyzers)
Oxygen electrode has been the subject of extensive investigations in the present work, since the oxygen electrode is the main factor related to energy efficiency. This study mainly explores the development of electrode/membrane materials and their application in electrolysis to improve the oxygen evolution reaction. A methodology for preparing materials in an efficient, rapid and cost effective manner has been developed to improve performance of the systems. The overall aim was to increase the current densities at a particular voltage so that hydrogen generation capacity is increased in comparison to existing materials with optimized processes.

1.7 RESEARCH OBJECTIVES

The driving force for this investigation is to design newer class of materials for water electrolysis with the aim to improving the performance of the electrolyzers (in terms of the operating current density at lower voltages) and thus reducing the cost. The objectives of this research are:

1. To develop and characterize a ternary nickel alloy electrodes by using four methods of electrodeposition viz., direct current electrodeposition, pulse electrodeposition, sono assisted direct current electrodeposition and sono assisted pulse electrodeposition for AWE application.

2. To improve the efficiency of an AWE process Citric acid (CA) has been chosen as an additive which was added directly into the electrolyte during the electrolytic process.

3. To develop a zero gap alkaline anion exchange membrane (AEM) based water electrolyzer based on the electrodes developed and graphene oxide modified electrodes.

4. To compare the properties of graphene oxide (GO) and carbon nanotubes (CNT) based sulphonated polysulphone
(SPSF) nanocomposite membranes in water electrolysis application.

5. To prepare composite membranes of caesium salts of silicotungstic acid (CsSiWA) and inorganic fillers (titanium dioxide (TiO₂) / silicon dioxide (SiO₂) / zirconium dioxide (ZrO₂)) with partially sulfonated poly(ether ether ketone) (SPEEK) polymer via. Sol gel process and study the properties of the electrolyzer with electrodes prepared by impregnation-reduction (I-R) and conventional brush coating method.

Therefore this dissertation specifically addresses the optimization of materials such as electrodes and membranes for hydrogen production, as an approach to reduce the capital and operating costs. A material design approach was used to produce products with high chemical and electrochemical stability at the temperature of operation of the cells. The scope of the dissertation was thus to design new routes to prepare electrode/membrane materials for electrolyzer systems to achieve high energy efficiency combined with a high production capacity.

1.8 SCOPE OF THE WORK

The topic of the dissertation is focussed exclusively upon hydrogen production by electrolysis of water which includes water and alkaline water as electrolytes. This dissertation specifically addresses the optimization of materials such as electrodes, membranes and stabilisers for gas production, as an approach to reduce the cost of hydrogen. Both aqueous and solid polymer electrolyte environments were evaluated in the present work. There are five parts in this thesis study.
In the first part, the preparation and characterization of tertiary alloy coating for use in alkaline water electrolysis is discussed. The electrodes were prepared by different types of electrodeposition methods such as direct current electrodeposition, pulse electrodeposition, sono assisted direct current electrodeposition and sono assisted pulse electrodeposition. The details of the preparation of the electrodes are described in terms of plating current density, pulse duty cycle and temperature. The oxygen evolution characteristics of the electrodes were evaluated by cyclic voltammetry and potentiodynamic sweep studies. The electrochemical parameters were calculated based on the studies carried to optimise the electrode fabrication technique.

Second part details the effect of an additive citric acid when added to the electrolyte on the oxygen evolution reaction. The quantity of the additive was varied between 0.1 and 1 wt. % in the electrolyte. The additive was found to decrease surface tension, improve catalytic activity, improve performance by forming a complex with the alloy electrode thus stabilising the active form of the catalyst. Moreover the resulting stabilizer displayed an increase in the current density of about 25% at the temperature of 30°C when compared to that of studies without the additive.

Third part describes the performance of a GO modified non-noble metal based electrode in a zero-gap alkaline water electrolyzer. The electrolytic cell was fabricated using a polystyrene based anion exchange membrane and a ternary alloy electrode of Ni as cathode and oxidized Ni electrode coated with GO as anode. The electrochemical activity of the GO modified electrode was compared to that of the uncoated electrodes. Long term stability tests in the electrolysis cell were studied by continuous 20h operation at 80°C.

The fourth part consists of preparation of nanocomposite membranes with GO and carbon nanotubes in a sulfonated polysulfone
matrix. The composites membranes were evaluated for their uniform distribution of the nanomaterials and their application in membrane based water electrolyzers.

The fifth part describes the development, characterization and application of sulfonated membranes based on polyether ether ketone, cesium salt of silicotungstic acid and transition metal oxides based nanocomposite membrane for water electrolysis application. Titanium dioxide, silicon dioxide and zirconium dioxide were chosen for preparation of the membranes. The electrodes for evaluation in water electrolysis application were prepared by impregnation-reduction and conventional brush coating methods. The performance of the membranes were evaluated and compared to that of Nafion® membranes.