INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 14934–14942

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journal homepage: www.elsevier.com/locate/he

Graphene oxide modified non-noble metal electrode for alkaline anion exchange membrane water electrolyzers

S. Seetharaman [a,b], R. Balaji [a], K. Ramya [a,*], K.S. Dhathathreyan [a], M. Velan [b]

[a] Centre for Fuel Cell Technology, International Advanced Research Centre for Powder metallurgy and New Materials (ARCI), II Floor, IIT-M Research Park, No. 6, Kanagam Road, Taramani, Chennai 600 113, Tamilnadu, India

[b] Department of Chemical Engineering, A.C. College of Technology, Anna University, Chennai 600 025, India

ARTICLE INFO

Article history:
Received 20 May 2013
Received in revised form
28 August 2013
Accepted 9 September 2013
Available online 9 October 2013

Keywords:
Water electrolysis
Alkaline water electrolyzer
Anion exchange membrane
Graphene oxide
Hydrogen production

ABSTRACT

This paper reports the performance of a graphene oxide modified non noble metal based electrode in alkaline anion exchange 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 graphene oxide as anode. The electrochemical activity of the graphene oxide modified electrode was higher than the uncoated electrode. The anion exchange membrane water electrolyzer (AEMWE) with the modified electrode gave 50% higher current density at 30 °C with deionised water compared to that of an uncoated electrode at 2 V. Performance was found to increase with increase in temperature and with the use of alkaline solutions. The results of the solid state water electrolysis cell are promising method of producing low cost hydrogen.

1. Introduction

Hydrogen has been proposed as a potential fuel to cater to the future energy needs as it does not release pollutants (particulates and carbon dioxide) at the point of use and hence is an environmentally cleaner source of energy. Hydrogen can be produced by steam reforming of fossil fuel, electrolysis of water or by other methods. As steam reforming process produces large amount of pollutants, electrolysis of water has received a lot of attention. Electrolysis of water may be carried out using alkaline and acidic electrolytes. Alkaline water electrolysis offers many advantages as it is a well established process that uses non noble metal based catalysts which are cost effective and with which multicell stacks may be built for commercial applications [1]. The disadvantages of the system include use of corrosive electrolyte, operation at low current densities and low pressure (<400 mA/cm^2 and ambient pressure) [1]. Research on the use of polymer electrolyte membranes that can conduct OH^- ions has attracted a lot of attention in the recent years [2–4]. Polymer electrolyte membrane based electrolyzers offer the advantage of low gas cross over rate resulting in high purity product gases due to the solid structure of the membrane. They can be operated at high pressures. Further, membrane based electrolyzers offer

* Corresponding author. Tel.: +91 44 66632710; fax: +91 44 66632702.
E-mail addresses: ramya.k.krishnan@gmail.com, ramyais@rediffmail.com (K. Ramya).
0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.09.033

compact designs when the cells are stacked and the cells/stack may be operated under varying loads based on the requirement.

Thin hydroxyl ion conducting membranes which offer high conductivity for the transport of hydroxyl ions are required for operation of the alkaline cells at high current densities and at high pressure. Hydroxyl ion conducting membranes based on Poly(ether ether ketone), polysulphone, polystyrene are also currently being researched [5–9]. Research and development on alkaline ion exchange membranes are focused on the improvement of transport properties for hydroxyl ions by increasing the density of fixed cationic groups, increasing the stability of the cationic group to nucleophilic substitution reactions, introduction of fluorine containing groups to improve stability etc [10].

Recently, Cao et al. [11] have prepared a quaternary ammonium grafted polyvinyl benzyl chloride membrane for use in alkaline anion exchange membrane water electrolyzers (AEMWE) with $Cu_{0.7}Co_{2.3}O_4$ and nano Ni powder as oxygen and hydrogen evolution catalyst respectively. A current density of 100 mA/cm^2 was obtained at 1.99 V and 55 °C. Wu et al. [12] have reported fabrication of a polymethacrylate-based quaternary ammonium OH^- ionomer binder for non precious metal alkaline AEMWE and have reported a performance of 100 mA/cm^2 at 1.9 V with deionized water. A stable performance at 1.8 V for 300 min has also been reported at a current density of ~50 mA/cm^2. Xiao et al. [9] have fabricated a water electrolysis cell using an MEA made of quaternary ammonia polysulphone membrane using Ni–Fe anode and Ni–Mo cathode. Long et al. [13] have reported a solid state water electrolysis cell with an alkaline membrane using iridium oxide as anode catalyst and Pt black as cathode catalyst. The cell exhibited a current density of 399 mA/cm^2 at 1.8 V and 50 °C in the absence of any liquid electrolyte. It has been reported that some hydroxide containing polymers show promising performance in water electrolysis cells when in contact with aqueous alkali [4]. The use of alkaline solution can increase the corrosion problems in the cell and auxiliary equipment. Improvement in the performance in the presence of alkali solution could be due to improvement in membrane conductivity or due to contact/interface improvements between the membrane and the electrode assemblies [4].

Several oxides and hydroxides based on Nickel have been widely studied as stable electro catalysts for alkaline water electrolysis (AWE) [14–16]. It has been proven that selected coatings on nickel such as Pt, NiMo, RuO_2 etc improve the performance of the electrodes in alkaline water electrolysis [17]. Graphene a two-dimensional sheet composed of sp^2 bonded carbon atoms with one-atom-thick carbon arranged in hexagonal pattern (like a honeycomb) have high surface area, superior conductivity with high chemical and thermal stability [18]. Treatment of graphite (3D structure of stacked graphene sheets one on top of other and linked to each other by weak intermolecular forces) with strong oxidizing agents (exfoliates and oxidizes) produces graphene oxides in which the hexagonal carbon atoms in the edges contain several functional groups such as carboxy, hydroxyl, carbonyl etc. on the surface [19]. It has been shown that graphene sheets can give rise to an extraordinary modification to the electrocatalytic properties of Pt cluster on their surface [20]. Graphene/metal oxide/transition metal oxide composites with improved electrocatalytic properties have been developed and used for application in Li ion batteries, supercapacitors, electrochromic windows etc [21–23]. The improved activity may be due to the stabilization of active form of the catalyst by bond formation between the metal ions and carboxyl groups of the graphene oxide through electrostatic attraction. Li et al. [24] prepared MoS_2 nanoparticles on reduced graphene oxide sheets by solvothermal synthesis for studying the electrocatalytic activity in hydrogen evolution reaction. The improved properties were attributed to the increase in catalytic edge sites and excellent electrical coupling to the graphene network.

Literature studies have thus shown that Ni based electrodes are suitable for alkaline water electrolyzers. Further studies on graphene have shown that enhancement in electrochemical properties can be achieved by the use of graphene/graphene oxide in the electrodes. The objective of the paper thus was to develop a zero gap alkaline anion exchange membrane based electrolyzer which incorporates Ni based catalysts that have been modified with graphene oxide and study its properties. The effect of the modified electrode on performance in alkaline water electrolyzer was optimized in terms of temperature, concentration of the alkali solution and stability.

2. Experimental

2.1. *Materials*

Selemion AMV a commercially available anion exchange membrane from Asahi Glass Co. Ltd. was used to fabricate the alkaline water electrolyzer cells. This is a copolymer synthesized from styrene, Chloromethyl styrene and divinylbenzene containing quaternary ammonium groups. The structure of the polymer has been depicted in Fig. 1. These membranes are supplied with chloride ion as counter ion. The thickness of these AEM membranes is ~120 μm. Prior to use the membranes are soaked in aqueous alkali solutions (3 M KOH for 24 h at 30 °C) to convert them into OH^- form. The membranes were washed

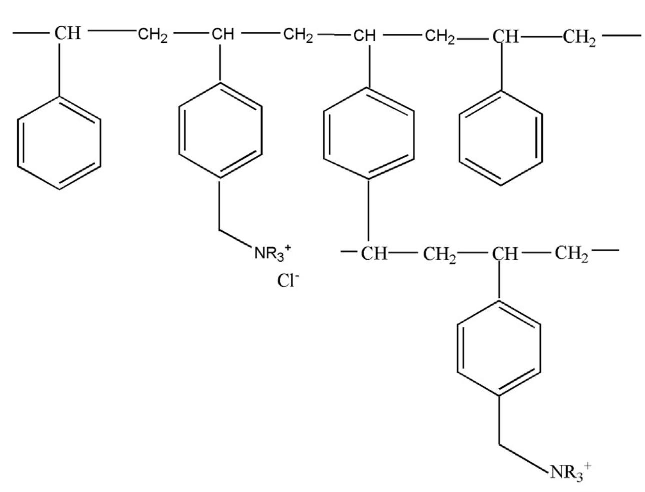

Fig. 1 – Structure of the AEM.