

Production Of Hydrogen By Anion Exchange Membrane Using AWE

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Abstract: This paper reports the performance of nickel oxide based electrode in alkaline anion exchange membrane water electrolysis. The membrane used is polystyrene based alkaline membrane and the electrode used is Nickel as cathode and Nickel oxide as anode. The electrochemical activity of the Nickel oxide is high compared to uncoated electrode. The AWE membrane electrode gave high current density at 300C with deionised water. The performance tends to increase by changing the temperature and alkaline solution. This results in increasing hydrogen production and be a promising technology in the future.

Keyword: AWE, Electrolysis, Hydrogen, Anion Exchange membrane, Alkaline, MEA, Deionised Water.

1 INTRODUCTION

Hydrogen plays an important role as an energy carrier for sustainable development [1-5]. It can be used in fuel cells to generate electricity, with water as the only product [6]. Besides, hydrogen is considered as the lightest element and any leakage of hydrogen gas can disperse quickly and thus hydrogen is believed as safe as other commonly used fuels [7]. Presently, hydrogen can be economically produced from hydrocarbon reforming, which is neither renewable nor clean from the life cycle point of view [6-8]. Powered by solar energy, hydrogen can be produced from water via photo catalysis, thermo chemical cycles, and water electrolysis [7-10]. These methods offer renewable and clean production of hydrogen fuel and, therefore, have attracted increasing research interests in recent years. So far, the efficiencies of photo catalysis and thermo chemical cycles are still too low to be economically competitive. Water electrolysis is hence the most promising technology for large-scale hydrogen production [5,9]. Compared with traditional alkaline electrolysis, in which potassium hydroxide (KOH) aqueous solution is used as the electrolyte, the advantages of the alkaline electrolyzer include simplicity, proven technology, and no special requirements. Disadvantages of the alkaline electrolyzer are the low efficiency and low current density [11-12]. In the present work, anion exchange membrane is used to increase the rate of the reaction and to make the cell compact in size. Alkaline water electrolysis offers many advantages as it is a well established process that uses metal based catalysts which are cost effective and with which multicell stacks may be built for commercial applications [13]. The disadvantages of the system include use of corrosive electrolyte, operation at low current densities and low pressure (<400 mA/cm² and ambient pressure) [13]. 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 [14-18]. 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 [19]. Several oxides and hydroxides based on Nickel have been widely studied as stable electro catalysts for alkaline water electrolysis (AWE) [20-22]. It has been proven that selected coatings on nickel improve the performance of the electrodes in alkaline water electrolysis [23]. Literature studies have thus shown that Ni based electrodes are suitable for alkaline water electrolyzers. The objective of the paper thus was to develop a zero gap alkaline anion exchange membrane based electrolyzer with Ni based catalysts. 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

Selemon 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. These membranes are supplied with chloride ion as counter ion. The thickness of these AEM membranes is 120 μ m. Prior to use the membranes are soaked in aqueous alkali solutions (1MKOH for 24 h at 30°C) to convert them into OH⁻ form. The membranes were washed free of alkali and stored in distilled water till use. The Nickel foam had a thickness of 140 μ m, pore diameter of 0.35 mm.

2.2 Preparation of electrodes

The nickel oxide was prepared by Glycine nitrate method in 2:1 ratio. It is calcined for about 400°C in open air. Nickel nitrate get combusted and form Nickel oxide. The NiO ink is prepared by mixing with the ionomer with the sample and the NiO ink was painted using brush coating technique [25]. In order to study the activity of the various electrodes prepared, chronoamperometric studies were carried out by using three electrode systems with NiO as working

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electrode, Hg/HgO as reference electrode and platinum as counter electrode in 1 M KOH solution at a potential of 1 V.

2.3 MEA design and electrolyzer operation

The electrolysis was carried out at a temperature of 30°C using a zero gap cell fabricated with anion conducting membranes. The nickel oxide electrodes prepared were used as the anode and cathode. The electrolytic cell was assembled with the two foam pressed up against the membrane and placed between two teflon coated fibre reinforced gaskets of thickness 0.22 mm and inserted between two platinised titanium plates with straight parallel grooves at the centre. The above items were clamped together using nuts and bolts by applying uniform torque of 30 lbf inch. The cell had provision for heating, temperature control and removal of products. The electrolysis was conducted to generate hydrogen at the cathode, by applying current across the two terminals of the electrolyzer using a DC power supply unit having constant current and constant voltage mode provisions. All current densities reported in this paper are based on the geometric area of the electrodes. All the experiments were repeated thrice to verify the reproducibility of the results.

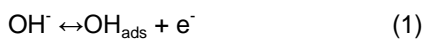
2.4 Characterization studies

The surface morphology of the electrodes was observed by 30 kV Hitachi SU1500 Scanning Electron Microscope (SEM). The electrochemical impedance spectra (EIS) were measured in a typical frequency range from 1 MHz to 0.001 Hz with 5mV excitation amplitude using a Solartron 1400 eight-channel multistat and computer interface and Z View software. Polarization experiments were carried out with a power supply unit that could pass direct current. Two multimeters were used to monitor the amount of current and voltage supplied to the electrolyzer. The catalytic activity of various coating materials for OER was assessed by recording chronoamperometry response on electrodes at a temperature of 30°C in 1M KOH.

3. RESULTS AND DISCUSSION

3.1 Electrode activity

The activity of the bare Nickel is the least and it improves on using various coating techniques. The order of their activity towards oxygen evolution reaction at 30°C is bare Ni < NiO. Steady state values were obtained immediately after the start of the reaction itself. The NiO electrode shows the highest current density for OER reaction. The oxygen evolution reaction mechanism may be depicted by Ref. [24].



The recombination of the O_{ads} is a fast step [24]. On the surface of NiO the electrochemical reaction taking place may be illustrated as

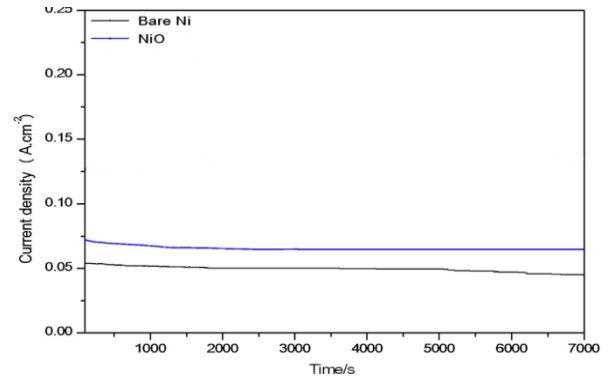


Fig. 1 Chronoamperometric curve for bare Nickel and Nickel oxide

NiOOH acts as a catalyst for oxygen evolution reaction. Adsorption of OH^- increases due to electrostatic interaction and improves the electrochemical activity [25]. The Nickel oxide on the surface may further improve the contact area between the electrode and the electrolyte as it forms a continuous phase between them and improving the electrochemical properties.

3.2 Polarisation studies

The key element for enabling a high performance in zero gap electrolysis cells is the MEA, which consists of anode electrode, AEM and cathode electrode. The MEA provides the essential interfacial contact between the membrane (electrolyte) and the electrodes to facilitate the electrochemical reaction in the electrolytic cell. In an alkaline water electrolysis cell, water is consumed at the cathode and reduced to produce hydrogen gas and hydroxide ions. The OH^- ions are then conducted through the AEM, to the anode. At the anode, OH^- ions are oxidized to produce oxygen gas, water, and electrons

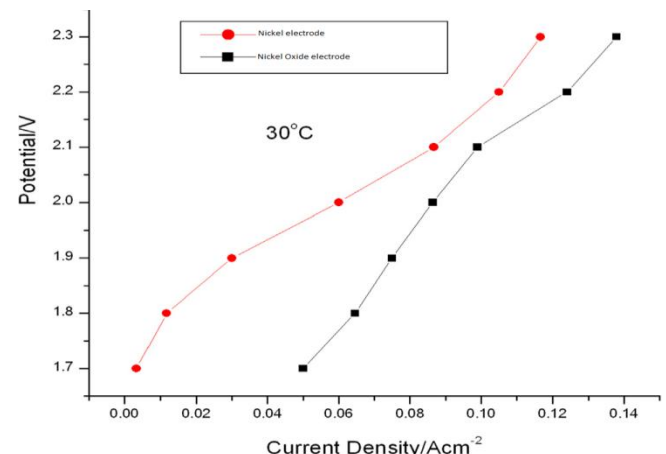
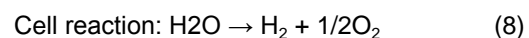
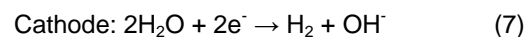
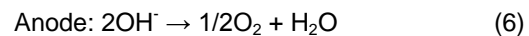


Fig. 2 Polarization curve for anion exchange membrane water electrolysis cell with various electrodes and deionised water at 30°C.

The result showed that the onset of electrolysis starts at a voltage of 1.6 V. A current density of 90 mA/cm² and 60 mA/cm² are obtained at 2.0 V and 30°C for the NiO and the Ni electrodes respectively. The performance of these cells is very modest compared to the commercial cell performance of 150 mA/cm² obtained at 1.9 V operating with 1M alkaline solutions at 80°C [26].

3.3 Effect of temperature

The cell performance increased with increase in temperature due to enhancement of electrode kinetics, ion transport, and also the conductivity of the membrane. The activation overpotentials decrease with increasing temperature leading to a better performance at high temperatures. The polarization curve is linear showing that there is sudden change in performance with temperature. The comparison of the performance curves of Ni and the NiO electrodes show that high current densities are achievable with electrode modifications, temperature and improvements in the conductivity at the interface of electrode and the membranes.

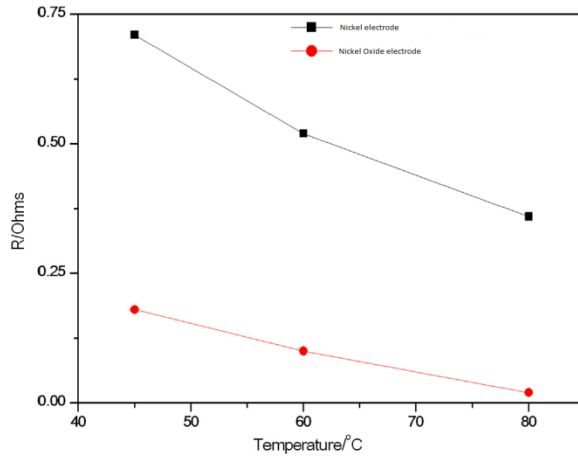


Fig. 3 Effect of temperature on resistance of Ni and NiO electrode.

3.4 Stability of the electrode

Stability of the electrode has been studied by continuous operation in constant voltage mode for 24 h. It can be seen that stable performance can be obtained with less fluctuations in current density with both the type of electrodes. The present study has shown a method to achieve high performance in alkaline water electrolyzers with anion exchange membranes by a simple coating technique. With pure deionised water based alkaline membrane based water electrolyzers as a long term goal, the present cell architecture with zero gap configuration was developed with NiO electrodes. The high performance obtained shows a lot of promise towards achieving the goal.

4. CONCLUSION

A metal based alkaline anion exchange membrane water electrolyzer was fabricated. The NiO electrode had lower resistance and provided higher surface area for contact with the membrane improving the electrochemical properties. The resistance of the electrodes was found to decrease with increasing temperature. The anion exchange membrane water electrolyzer with the modified electrode

gave a current density of 90 mA/cm² at 30°C and with deionised water compared to 60 mA/cm² for the conventional electrode at 2 V. Performance was found to increase with increase in temperature and with the use of alkaline solutions.

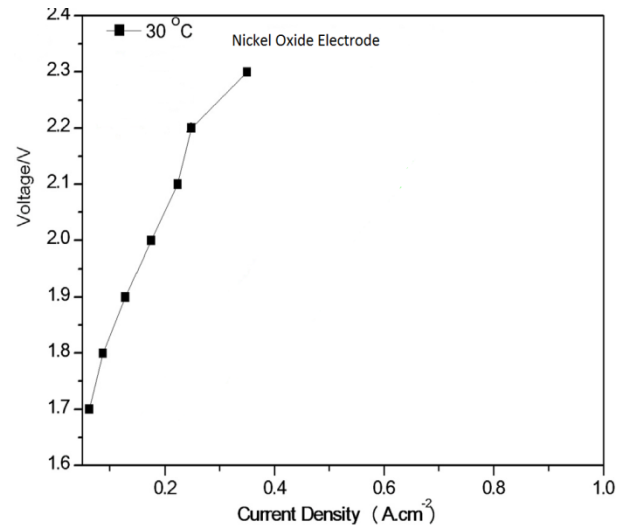


Fig 4. Effect of temperature on NiO anion exchange membrane water electrolyzer in 1M KOH electrolyte.

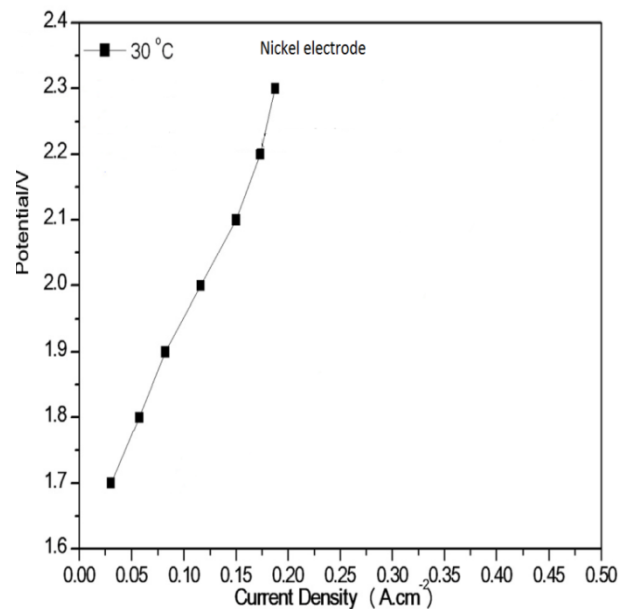


Fig 5. Effect of temperature on Ni anion exchange membrane water electrolyzer in 1M KOH electrolyte.

A maximum performance of 400 mA/cm² was obtained at 1.9 V with 1M KOH solution as electrolyte at 80°C with modified electrodes compared to 260 mA/cm² with Ni electrodes. Stable performance was obtained when the electrodes were operated for 24 h at high current densities. Further improvements in the performance are envisaged with incorporation of ionomers in the electrode to improve ion transport between the electrode and the membrane. Membrane durability, conductivity and changes in the conductivity are yet to be studied to improve the technology similar to that of current state of the art commercial alkaline water electrolyzers.

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