

STUDIES ON THE EFFECT OF ELECTROLYTE CONCENTRATION ON ALKALINE ELECTROLYSIS AND ION EXCHANGE MEMBRANE WATER SPLITTING FOR PRODUCTION OF HYDROGEN

Biswajit Mandal¹, Amalesh Sirkar², Parameswar De³, Sunil Baran Kuila⁴

¹* Assistant Professor, Department of Chemical Engineering, Haldia Institute of Technology, Haldia - 721 657, West Bengal, India.

² Professor, of Chemical Engineering, Haldia Institute of Technology, Haldia - 721 657, West Bengal, India

³ Professor, Department of Chemical Engineering, University of Calcutta, 92 A.P.C. Road, Kolkata - 700 009, India.

⁴ Associate Professor, of Chemical Engineering, Haldia Institute of Technology, Haldia - 721 657, West Bengal, India

Abstract

The rate of hydrogen production increases with increase in concentration of potassium hydroxide and sodium hydroxide solution as an electrolyte. It can be attributed to the increase in electrical conductivity of the solution due to increase the KOH and NaOH concentration in the solution. Maximum 3 (N) concentrations of both electrolytes were investigated within the same range of applied DC voltage. KOH solution as electrolyte showed 14.77% higher performance than NaOH solution in terms of hydrogen production rate at extreme conditions within the present limits of investigation. Effect of concentration of NaOH on electrolysis was comparatively better than KOH solution within the same range of concentrations (0.01–3.0 N). Investigation on membrane water splitting resulted enhancement of hydrogen production rate from 1.33cc/min to 5.69 cc/min using amide membranes of different composition ranging from 25–75 % acrylamide content in chemically modifying polyvinyl alcohol matrix with poly(Acrylic acid-co-Acrylamide).

Keyword: Alkaline Electrolysis, Membrane Electrolysis, Electrolytic Hydrogen, Concentration Effect, PEM Water Splitting.

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1. INTRODUCTION

Hydrogen, a clean energy carrier, can produce from renewable sources. Hydrogen production by alkaline electrolysis is one of the promising avenues among all technological processes. In electrolytic cell, electrodes are the key physical part of the system. Inert electrodes just use its surface for neutralization of ions to take place. Platinum, carbon and stainless steel are generally used as inert electrodes. Electrolysis is usually assisted by alkaline solution namely aqueous KOH or NaOH solution. The efficiency of electrolysis of water is limited mainly due to the internal resistance between electrodes. Upon the introduction of direct current to the electrolyzer, electrons start moving from the surface of an electrode through the electrolyte solution and neutralize at the surface of the other electrode. Different variables such as the electrodes resistivity, conductivity of the electrolyte, and the reaction between electrodes surfaces and electrolyte contribute internal resistance of an electrolyzer. Hence, the equivalent resistivity is a function of the variables namely space between electrodes, size and alignment of the electrodes forcing the bubbles to leave the solution, electrode geometry, electrode material, separator material, applied voltage waveform and electrolyte concentration [1].

Pure water at 25°C could release hydrogen and hydroxide ions in concentration of 1×10^{-7} moles per liter. Conductivity

of water for electrolysis improved by the addition of strong electrolytes. Electrolyte solution increases the quantity of ions in the solution, and thereby decrease the average distance and time for ions at the electrodes to encounter ions of the opposite charge. Water has a dielectric constant of about 80 at room temperature. The cations of the electrolyte solution are attracted to the slightly charged oxygen atoms of the water and simultaneously electrolyte's anions are attracted to positively charged hydrogen atoms of water. The degree of dissociation of electrolytes is quantitatively defined by dissociation constants.

Hydroxides of alkali metals generally dissociate in water and create small amounts of metal buildup on the cathode. Theoretically, an ion conducts electricity in an infinitely dilute solution of electrolyte most efficiently per mole. This situation could be well understood by considering an electric potential between two electrodes in aqueous solution containing only one molecule of monoprotic electrolyte. Cations and anions are attracted to the respective electrodes and the potential difference propels the ions across the electrodic gap. The ions of opposite charges are attracted to each other between the electrodes, resulting to slowdown and deviate from their original line of movement. But the force of attraction between the opposite ions never overcomes their attraction towards electrodes and thus continues to move onto their respective electrodes. The

mutual attractions between the ions only influence the reaction to take place at an exceedingly slow rate. Therefore the most efficient ionic conduction of electricity per mole occurs when ions are infinitely dilute or by minimizing the ionic interaction by any means [2]. Another attempt for hydrogen production through water splitting is by ion exchange membrane water splitting. Since a moving charge in an electrolytic cell is similar with electric current, the ionic membrane acts as a conductor of electricity. A typical proton exchange membrane sold by DuPont under the trade name nafion[®], is generally used in fuel cell and other ion exchange activity through membrane. Apart from fuel cell application, proton exchange membrane can also be used for water splitting to generate hydrogen. It has many advantages over conventional electrolyzers normally use aqueous alkali solution as electrolyte. Nafion[®] is a solid proton exchange membrane and noncorrosive in nature. Another benefit of proton exchange membrane is its excellent gas separation ability, thus allows water to permeate almost to the exclusion of H₂ and O₂. Unlike conventional polymers which are hydrophobic, nafion[®] is a very expensive material. It must be kept humidified constantly otherwise its conductivity deteriorates gradually [3]. The key property of proton exchange membrane is its conductivity due to presence of negatively charged group. In the present investigation, water splitting was carried out in laboratory made polyvinyl matrix with poly(acrylic acid-co-acrylamide) [4]. The amide group in the membrane can exhibit similar kind of ionic properties, eventually membrane can be utilized in electrolyzer or in fuel cell [5].

Platinum is considered as best catalyst for electrolysis of water due to its moderate adsorption strength of the intermediates and also due to its lowest over-voltage among all metals. But due to its higher cost, the preferred operation of the electrolyzer at high current, ultra-fine platinum particles generally used either directly on the membrane or on the electrode support plate. It was reported that 1–3 Amp. current per square centimeter could be obtained using 3 milligrams of Pt spread over the same area [6,7]. The present work was carried out in laboratory made proton exchange membrane namely PVOH matrix with poly(acrylic acid-co-acrylamide) using 3% Pt in activated carbon as cathodic and anodic catalysts.



Fig-1: Experimental set-up for alkaline electrolyte water splitting

2. EXPERIMENTAL

2.1 Set-up and procedure

Studies on electrolyte concentration were carried in a double compartment electrolyzer of capacity 3 lit volumes. Fig. 1 shows the experimental set-up for the present investigation. In order to operate the electrolyzer at variable concentration of electrolyte, it was necessary to operate the electrolyzer at a constant temperature; hence it was kept in a thermostatic bath. Flat type graphite electrodes were used.

Measurements of current and voltage used in the operation were made by an ammeter (0–20 A) and a voltmeter (0–120 V) respectively. The volume of hydrogen gas was measured by downward displacement of saline water and the gauge pressure of produced gas was measured by a U-tube manometer connected with the gas line. In Search of an alternative Polymer Electrolyte Membrane for electrolyzer, fuel cell and regenerative fuel cell, an attempt was made to synthesize amide membrane. The objective of the application of membrane made of polyvinyl matrix with poly(acrylic acid-co-acrylamide) was twofold. By incorporation of poly(acrylic acid-co-acrylamide) in PVOH matrix, the crystallinity of PVOH membrane would be reduced and subsequently hydrophilicity as well as water permeability increased. Copolymerization of Acrylic acid and Acrylamide within the of polyvinyl alcohol matrix later on crosslinked using glutaraldehyde to synthesize semi interpenetrating network polymer (SIPN). Present work were carried out using three SIPN membranes with increasing amount of poly(acrylic acid-co-acrylamide) in polyvinyl matrix. The investigations were carried out using 25%, 50% and 75% amide membrane (Table 1). Fig. 2 shows the fuel cell type electrolyzer containing polymer electrolyte membrane for water splitting. The surface was loaded with platinum catalyst (3% Pt on activated charcoal).



Fig-2: Experimental set-up for polymer electrolyte membrane water splitting

The experiments to investigate the effect of percentage of amide in membrane on water splitting, it was important to install the membrane in a properly designed electrolyzer. The design of electrolyzer was quite similar to the fuel cell. Catalyst loaded membrane was sandwiched between two silicon rubber sheets. Thereafter it was again sandwiched between the grooved graphite plates inside facing the silicon rubber sheets and finally with two Perspex sheets. Arrangement was made for the passage of hydrogen and oxygen gases. Before DC electrical supply to the electrolyzer, it was important to check the chances of short circuits. Very dilute KOH (0.01 N) solution of volume 1 liter was to be filled in two limbs (Fig. 2) to ensure proper conductivity.

3. RESULTS AND DISCUSSION

The effect of concentration of potassium hydroxide on the electrolytic hydrogen generation process was investigated. To fulfill a comprehensive understanding of the effects of the concentration of electrolyte on the hydrogen production rate, two different electrolytes were examined. During test, the pair of electrodes was exposed to a DC volt ranging from 5 to 70 volts. Concentrations of electrolyte solution varying from 0.01(N) to 3.0 (N) were also tested. The rate of hydrogen production was measured at 32°C (room temperature) constant operating temperature. Figure 3 represents the increase of hydrogen production rate with increase in electrolyte concentration (KOH solution) at different applied DC voltages at constant 32°C operating temperature. It was found that the enhancement of hydrogen production rate was minimum (73.7%) at highest applied DC voltage (70 V DC) within the electrolyte concentration ranges between 0.01 (N) and 3.0 (N). Moreover, 78.95%, 90.46%, 103.4%, 108.47%, 171.74%, 270.78%, 330.05% and 646.84% improvement of hydrogen production rate were reported with corresponding applied DC voltages of 50, 40, 30, 24, 20, 12, 10 and 5 V DC respectively.

The trend in improvement of hydrogen production rate clearly indicates that electrolysis not only depends on the number of ions present in solution rather on their mobility in the solution. Gradual increase in electrolyte (KOH) concentration surely increased the number of ions in the solution which subsequently decreased the ion mobility due to hindrance.

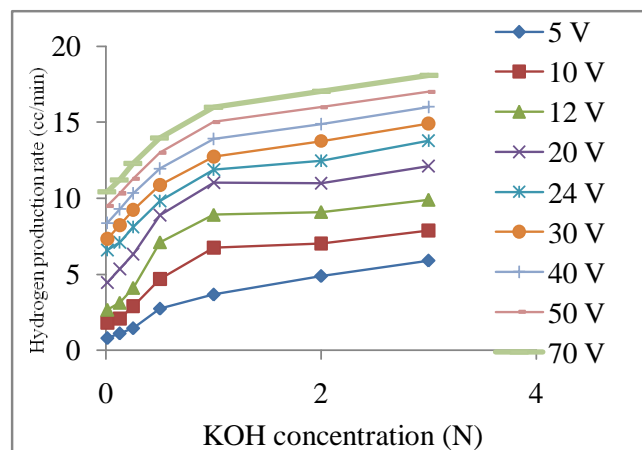


Fig-3: Hydrogen production rate vs. KOH solution concentration for different DC voltages at constant temperature (31±1)°C, pressure (atm.) and applied current of (2± 0.02) amp.

It was also found that the effect of electrolyte concentration at lower applied voltage of 5V DC was greater. Only 20.9% improvement of hydrogen production rate was found by changing electrolyte concentration from 2.0 (N) to 3.0 (N), while 39.24% improvement was recorded between 0.01 (N) and 0.125 (N) electrolyte concentration using 5 V DC applied voltage. In contrary, only 6.28% improvement was achieved between 2.0 (N) and 3.0 (N) electrolyte concentration and 7.58% was recorded between 0.01 (N) and 0.125 (N) electrolyte concentration using 70V DC applied voltage. This clearly indicates that the performance of electrolysis in terms of enhancement of hydrogen production rate was comparatively better at low electrolyte concentration ranges and at low applied voltages. This might be due to the fact that at higher concentration of electrolyte eventually release more number of ions in the aqueous medium and irregular interaction between cations-anions, cations-cations and anions-anions may have restricted the free movement of ions across the respective electrodes. It was logical to explain the fact that the higher applied voltage and higher electrolyte concentration led to higher overpotential loss and resulted greater rise in electrolyte temperature in comparison with lower applied voltage. Hence, dilute electrolyte solution and low applied DC voltages were considered as the better option [8].

Table 1. Composition of three different polymer electrolyte membranes for electrolyzer

Poly (Ac. A-co-Ac.Am) as % of PVOH	Acrylic Acid + Acryl Amide (gm)	Acryl Amide (gm)	Acrylic Acid (gm)	MBA (2 wt% of Acryl Amide) (gm)
25	1.25	1.1349	0.1151 (0.11ml)	0.0227
50	2.50	2.2698	0.2302 (0.22ml)	0.0454
75	3.75	3.4047	0.3453 (0.33ml)	0.0681

A perusal of Figure 4 reveals that the effect of electrolyte concentration (NaOH solution) on rate hydrogen production was observed to follow the same trend as with variable KOH concentrations but the magnitudes were comparatively smaller. It was found that, the enhancement of hydrogen production rate was minimum (101.92%) at highest applied.

In contrary, the improvement of hydrogen production rate was 852.38% at lowest applied DC voltage (5 V DC) within the same range of electrolyte concentrations as mentioned above. Moreover, the enhancements of hydrogen production rate for different applied voltages like 10, 12, 20, 24 30, 40, and 50 V DC were reported 397.32%, 327.95%, 232.34%, 113.66%, 110.95%, 107.41% and 104.92% respectively, and the magnitude of improvement lies within the range of maximum and minimum applied voltage as stated above. In a comparison for suitability between KOH and NaOH electrolytic solutions, it was noticed that, the KOH always resulted with higher hydrogen production rates at every conditions.

On the contrary, the enhancement of production rate was reported higher in case of NaOH. This might be due the fact that, the solubility of KOH was higher than NaOH (121g/100ml water for KOH and for NaOH it was 100g/100ml) and the dissociation constant was also higher for KOH (p_{Kb} value of NaOH is 0.2 and 0.5 for KOH). In addition, the above mentioned fact might be explained by the reason that the water molecule in hydration cell of sodium ion was orientationally more ordered than potassium ion [9].

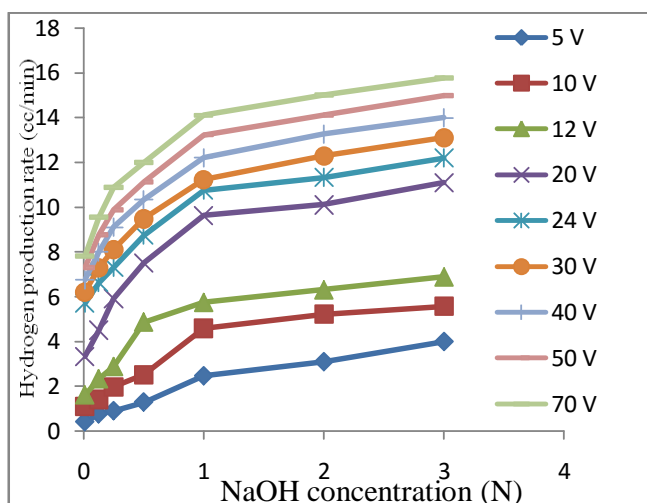


Fig-4: Hydrogen production rate vs NaOH solution concentration at different applied DC voltage at constant operating temperature (32°C) and applied current (2 A).

The dissociation energy of NaOH was comparatively more, and it could be justified by the magnitude of maximum/minimum hydrogen production rate (15.77 cc/min and 0.42 cc/min), which was quite less than KOH solution (18.10 cc/min and 0.79 cc/min). Therefore, KOH was considered as the better electrolyte for hydrogen production at any ranges of concentrations and applied voltage comparatively with NaOH.

Again, the polymer electrolyte membrane water splitting for hydrogen production was represented in Table 2. It reveals an important role of amide membrane in the area of membrane water splitting, and rate of hydrogen production was increased (1.33–5.69 cc/min) with increase in percentage of acrylamide in polymer membrane. The 75% amide membrane showed a remarkable performance in comparison to 25% in terms of hydrogen production rate. One of the plausible reasons behind this improvement may be the high conductivity of 75% amide membrane. Steady increase in hydrogen production rate with increase in amide percentage in membrane also demanded the experimentation with further higher percentage of amide membrane. It was investigated with 90% amide contentment of membrane, but it repeatedly failed because of its low mechanical strength and quick swelling tendency. Moreover 75% amide membrane exhibits satisfactory mechanical strength and swelling properties. Hence 75% membrane of poly(acrylic acid-co-acrylamide) in polyvinyl matrix was considered as the best one within the present limit of investigation.

Table 2. Effect of different polymer electrolyte membrane using 3% Pt in activated carbon as cathodic and anodic catalysts on water electrolysis at 32°C temperature

Polymer electrolyte membrane (% of Acrylamide)	Applied DC voltage (V)	Applied current (A)	Average hydrogen production rate (cc/min)
25	12	2	1.33
50	12	2	1.87
75	12	2	5.69

4. CONCLUSION

The present research is aimed to conduct experimental investigations on the effect of concentration of alkaline and alternative proton exchange membrane water electrolysis for the purpose of hydrogen production. The experimentation covered the effects of voltage, solution concentration, and the composition of membrane on the characteristics of alkaline and membrane water electrolysis. Both KOH and NaOH solutions showed increase in rate of hydrogen production with increase in concentration and applied voltage, and effect of concentration on electrolysis was greater in case of NaOH comparatively with KOH solution. In membrane electrolysis, it was also reported to increase hydrogen production rate with increase in amide content in PVOH matrix with poly(Acrylic acid-co-Acrylamide).

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BIOGRAPHIES



Biswajit Mandal is working as assistant professor in Chemical engg. Department at Haldia Institute of Technology for ten years. Email Id: bmandal_1977@rediffmail.com



Prof. Amalesh Sirkar is one of the renowned researcher on coal liquefaction process is working at HIT for 13 years. He owned seven patents on different fields including coal liquefaction process. Email Id: sirkar_a@hotmail.com



Prof. Parameswar De is Professor in the Department of Chemical Engineering at the University of Calcutta. He has engaged himself in teaching and research for over 30 years. His research areas include mass transfer & hydrodynamics in multiphase flow, biochemical & electrochemical engineering and reaction engineering. He has published papers in national and international journals. Email Id: parameswar_de@rediffmail.com



Dr. Sunil Baran Kuila is working as assistant professor in Chemical Engg. Department at Haldia Institute of Technology for ten years