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## Low cost hydrogen production by anion exchange membrane electrolysis: A review

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#### ABSTRACT

Anion exchange membrane (AEM) water electrolysis is a hydrogen production method that is achieved with an AEM, using electricity. One of the major advantages of AEM water electrolysis is the replacement of conventional noble metal electrocatalysts with low cost transition metal catalysts. AEM electrolysis is still a developing technology; therefore, with a view to using it to eventually achieve commercially viable hydrogen production, AEM electrolysis requires further investigation and improvements, specifically regarding its power efficiency, membrane stability, robustness, ease of handling, and cost reduction.

This review addresses state of the art technology of AEM electrolysis for hydrogen production. It also provides a summary of important research that has been carried out on membranes, electrocatalysts, and ionomers used in AEM electrolyzers, and the performance of such electrolyzers. The aim of this review is to identify gaps in AEM water electrolysis research and to make recommendations for future directions in AEM water electrolysis research.

#### 1. Introduction

Hydrogen has been identified as an alternative energy carrier to generate power for domestic, industrial, and automotive purposes [1–5]. It has great potential to change the world's energy sector, similar to what the computer and the internet achieved in the modern information technology sector [6]. Hydrogen offers many advantages as an alternative energy carrier, one of which is the energy content of hydrogen (118 MJ kg<sup>-1</sup> at 298 K), which is much higher than that of most fuels (e.g., gasoline 44 MJ kg<sup>-1</sup> at 298 K) [7]. Furthermore, the use of hydrogen can mitigate the issues associated with the use of fossil fuels: CO<sub>2</sub> and other greenhouse gases [8–13].

Hydrogen, in the form of hydrocarbons and water, is one of the most readily available elements on our planet. It can also be produced by various methods, such as thermal, electrolytic, and photolytic processes from fossil fuels, biomass, and water [14-18]. Water is considered a long-term source for the production of hydrogen due to its wide availability. The production of hydrogen from water can significantly reduce the depletion of fossil fuels and  $CO_2$  emissions [19-22].

Hydrogen can be produced from water by various methods,

including water splitting and electrolysis. Water splitting can be carried out by a thermochemical process, chemical conversion of biomass, and photocatalytic water splitting [23]. In water splitting, the water is disassociates into hydrogen and oxygen by a series of consecutive chemical reactions. The conversion occurs in the temperature range 800–2000 °C [24]. The heat required to convert water into hydrogen and oxygen may be generated by solar or nuclear power plants [25]. The major advantage of thermochemical method is that issues associated with various separation stages of the components can be avoided.

Photoelectrocatalytic hydrogen production is another promising method for the production of hydrogen from water [26]. Here, solar energy is converted into chemical energy, in the form of hydrogen, by using  ${\rm TiO_2}$  as a photocatalyst [27]. In this technology, the oxidation and reduction reactions occur simultaneously. The major disadvantages associated with the use of  ${\rm TiO_2}$  are wide band gap limits in the visible light region, frequent recombination of photogenerated electron-hole pairs, and higher overpotential for evolution [28]. Various steps have been taken to eliminate the disadvantages of  ${\rm TiO_2}$ ; it has been coupled with a carbon material, surface modified with adsorbents,

Abbreviations: AEM, anion exchange membrane; CCM, catalyst coated membrane; CCS, catalyst coated substrate; CV, cyclic voltammetry; DFT, density functional theory; DI, deionized; EIS, electrochemical impedance spectroscopy; GDL, gas diffusion layer; GDE, gas diffusion electrode; GO, graphene oxide; HER, hydrogen evolution reaction; I<sup>2</sup>MEA, integrated inorganic membrane electrode assembly; LDH, layered double hydroxide; LDPE, low density polyethylene; MEA, membrane electrode assembly; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; PEM, proton exchange membrane; PGM, platinum group metal; PSF, polysulfone; QAPS, quaternary ammonium functionalized polystyrene; VBC, vinylbenzyl chloride

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and  $TiO_2$  incorporated into nanoparticle [28]. Furthermore, an mesoporous  $TiO_2$  nanopowders has been prepared to enhance the catalytic activity, using cetyltrimethylammonium bromide as a surfactant-directing and pore-forming agent [27]. A metal-free, conjugated, semiconductor-based active polymeric graphitic carbon nitride g- $C_3N_4$  photocatalyst was developed for the photocatalytic  $H_2$  production [29,30]. The performance of g- $C_3N_4$  was enhanced by metal doping, metal deposition, and incorporation of a carbon compound [31] The photocatalytic performance was increased by an appropriate band structure formation at the heterojunction interface [32,33]. The modified Pt-loaded g- $C_3N_4$  exhibited a considerable improvement in the photoreduction [31].

Water electrolysis is a well-developed technology for the conversion of water into hydrogen and oxygen at low temperatures [34–37]. Electrolysis can be distinguished according to the type of electrolyte used in the electrolyzer. The two main water electrolysis technologies to produce hydrogen are alkaline electrolysis [38–42] and proton exchange membrane (PEM) electrolysis [43–45].

#### 1.1. Conventional electrolysis

#### 1.1.1. Alkaline electrolysis

In alkaline electrolysis, the most commonly used anode and cathode materials are nickel- and cobalt-based oxides, respectively, and the most commonly used liquid electrolyte is 30-40% KOH [46,47]. The electrolyte is circulated through the electrodes to provide the alkalinity required by the system. The anode and cathode chambers are separated by a porous diaphragm which conducts hydroxyl ions but not hydrogen and oxygen [46,48,49]. The diaphragms are made of ceramic oxides such as asbestos and potassium titanate, or polymers such as polypropylene and polyphenylene sulfide [50-53]. Typical alkaline water electrolysis operates at a current density of about 400 mA cm<sup>-2</sup>, at moderate temperatures of 70-90 °C, with a cell voltage in the range 1.85-2.2 V, and conversion efficiencies in the range 60-80% [54]. The advantages of alkaline electrolysis are that it does not depend upon a noble metal catalyst for the hydrogen production and handling is easy due to the relatively low temperatures [55].

#### 1.1.2. Proton exchange membrane electrolysis

In PEM electrolysis, the anode and cathode catalysts are typically  $\rm IrO_2$  and Pt black, respectively [56,57]. An acidic membrane is used as solid electrolyte (Nafion, DuPont) instead of a liquid electrolyte (The membrane conducts H $^+$  ions from anode to cathode, and separates hydrogen and oxygen that are produced in the reaction. The PEM electrolyzer can operate at a current density of 2000 mA cm $^{-2}$  at 90 °C, at about 2.1 V [58]. The kinetics of the hydrogen and oxygen production reaction in PEM electrolysis are faster than in alkaline electrolysis due to the acidic nature of the electrolyte and the metal surface of the electrodes [59]. PEM electrolysis offers safety due to the absence of caustic electrolyte [60]. One of the advantages of PEM electrolysis is the possibility of using high pressure on the cathode side, while the anode can be operated at atmospheric pressure [61].

## 1.2. Technology and cost problems associated with conventional electrolysis

During electrolysis, the oxygen produced at the anode is frequently in contact with the air. The liquid KOH electrolyte is highly sensitive to  $CO_2$  in the ambient air [62–64]; hydroxyl ions react with the  $CO_2$  and  $K_2CO_3$  is formed [62,65]:

$$CO_2 + 2OH^- \rightarrow CO_3 + 2H_2O$$

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$$

The formation of  $K_2CO_3$  reduces the performance of alkaline electrolysis. This is due to several factors.

- 1. This reaction reduces the number of hydroxyl ions present in the anolyte that are needed for the anodic reaction [66].
- 2. It also reduces the ionic conductivity of the electrolyte due to modification of the electrolyte composition [62].
- 3. The K<sub>2</sub>CO<sub>3</sub> precipitates in the pores of the gas diffusion layer (GDL), blocking ion transfer [67,68].

Therefore, the overall performance of electrolysis is reduced when using KOH liquid as an electrolyte. Furthermore, the hydrogen is stored at high pressure in the cathode compartment, which is not possible with liquid KOH [69-71].

On the other hand, although PEM electrolysis is efficient, the Nafion membrane, which is used in this type of electrolysis, is highly acidic (equivalent to  $10-20\%~H_2SO_4$ ) [72]; it therefore limits the choice of suitable catalyst material to the noble metals [73–75]. Nafion-based membranes that are commonly used in PEM electrolysis are very expensive. Furthermore, the conductivity of the membrane is reduced by the release of impurities from the feed water in the cathode compartment. Impurities bind to the active sites of the membrane in the membrane electrode assembly (MEA) [76–78]. Furthermore, the stack materials are more expensive than the stack materials used for alkaline electrolysis [79].

#### 1.3. Polymeric anion exchange membranes

Over the past few years, polymeric anion exchange membranes (AEMs) have been developed for electrochemical system applications. They offer benefits for both PEM and alkaline electrolysis, and for fuel cells [80]. AEMs have been used for alkaline fuel cells but to date not for electrolysis [81–84]. The main difference between alkaline and AEM electrolysis is the replacement of the conventional diaphragm with an AEM in alkaline water electrolysis. AEM electrolysis offers several advantages.

- 1. A transition metal catalyst is used instead of a noble metal (platinum group metal; PGM) as catalyst.
- Distilled water or a low concentration of alkaline solution can be used as electrolyte instead of concentrated KOH.
- The quaternary ammonium ion-exchange-group-containing membrane that is used in AEM electrolysis is less expensive than the Nafion-based membranes.
- The interaction between CO<sub>2</sub> and the AEM is low due to the absence of metal ions in AEMs.
- 5. Furthermore, the absence of a corrosive liquid electrolyte in this technology offers advantages such as the absence of leaking, volumetric stability, ease of handling, and a reduction in the size and weight of the electrolyzer.

Overall, AEM technology is low cost and highly stable for hydrogen production [85].

The specifications, advantages, and disadvantages of the major electrolysis techniques are summarized in Tables 1 and 2.

#### 1.4. Anion exchange membrane electrolysis

AEM electrolysis is a developing technology. Many research organizations and universities are actively involved in this research, largely due to its low cost and the high performance it offers [72]. However, compared to the other conventional electrolysis technologies, few research articles (<20) have been published on AEM electrolysis. AEM electrolysis still requires further investigations into the following, for example: power efficiency, membrane and catalyst stability, ease of handling, and reduction of cell cost [72,85]. Significant improvements

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