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ELECTROCHEMICAL WATER SPLITTING: A REVIEW OF THE VARIOUS MEMBRANES INVOLVED

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Abstract: Splitting water into its components, hydrogen and oxygen, is an essential part of the quest to produce green hydrogen. The necessity of this has immensely increased over time due to demand for cleaner energy sources to encourage sustainable means of hydrogen fuel generation. Every electrolyser has four basic components, a positive anode electrode, a negative cathode electrode, an electrolyte for ion transport and a DC power supply. Depending on the type of electrolyser, the electrolyte could be either a liquid electrolyte or a membrane electrolyte. The electrolyte plays a very crucial role in the overall electrolysis process since it is responsible for facilitating the transportation of ions from one electrode to another, producing the desired end product, which is hydrogen. Membranes play an essential role in ensuring the separation of the gaseous products. This review draws attention to the membranes involved in the water electrolysis process.

Keywords **– Hydrogen, Green Hydrogen, Electrolysis, Membrane Technology, Sustainability, Ion Exchange Membranes, SDG 7**

INTRODUCTION

With the aim of steering clear or at least drastically minimizing dependence on fossil fuel for energy production, hydrogen production has been highly encouraged, hence various avenues of generating hydrogen currently exist some more mature than others. Water splitting has been around as a method for hydrogen generation for quite some time now, but it still not on the same scale as its more developed counterparts especially the thermochemical processes including the widely used natural gas reforming technique which is responsible for 80% of the worlds hydrogen production[1]. Steam reforming produces carbon dioxide as a byproduct which is a greenhouse gas and it has been well established that greenhouse gases contribute exponentially to climate change. In an effort to save the planet for irreversible damage, ways on improving the efficiencies of renewable methods of hydrogen production are constantly being explored. In the case of water electrolysers, there are various types dependent on the electrolyte type. Namely alkaline, acidic and solid oxide water splitting. Liquid electrolytes as well as polymer electrolytes can be utilised in both alkaline and acidic environments. At significantly higher temperatures(usually above 1000°C), solid oxide ceramics that are ion conducting are employed. Of the three water splitting methods, alkaline water electrolysis and proton exchange membrane water electrolysis are commercially more mature[2,3].

Due to the cost involved in the production of proton exchange membrane electrolysers, compared to alkaline water electrolysers they are less economical mainly due to expensive catalyst such as iridium and platinum involved in their production. Although cheaper to produce, alkaline water electrolysers have rather low efficiencies. To overcome this drawback, anion exchange membrane water electrolysers which are alkaline water electrolyser and proton exchange membrane water electrolyser hybrids that utilise a setup similar to the proton exchange membrane water electrolyser but operate in an alkaline environment and employ less expensive non-noble catalyst usually nickel based[4,5].

Membranes act as separators in all types of electrolysers allowing certain species to go through while restricting others, electrolysers with liquid electrolytes require membranes for gas separation while those with membrane electrolytes need it for both ion transportation and gas separation. Membrane based electrolysers have excellent efficiencies hence make good electrolysers[6,7].

TYPES OF WATER ELECTROLYSER MEMBRANES

Alkaline Water Electrolysis

In alkaline water electrolysers, membranes are employed to decrease the distance between electrodes and at the same time, decreasing the chances of the produced gases mixing. The membranes need to have high OH- ion conductivity while being impervious to both hydrogen and oxygen. Furthermore, the membranes need to be adequately stable in alkaline environments with high pH levels of up to 14 which is extremely corrosive. There are various commercially available membranes, they all have different porosities and properties. Membranes are mostly divided into two groups, exchange membranes and microporous membranes. They both have the same main function which is to be permeable to ions while keeping the gases produced, hydrogen and oxygen separate. Their mode of operation differ, microporous membranes basically withhold that is bigger than a specific size while exchange membranes allow the transmittance of OH- ions with minimal resistance. The contemporary zero-gap electrolyser employs the newer ion exchange membrane while the conventional alkaline electrolysers usually use porous or microporous membranes[8–10].

A suitable gas separator requires a high level of gas separation, particularly at the current densities of operation since the possibility for an explosion is high if hydrogen is exposed to more than 4% oxygen[11,12]. Gas purities greater than 99.5% are desirable for use in conjunction with hydrogen fuel cells. Additionally, a separator needs to be resilient to extreme alkaline conditions, have low ionic resistance and relatively inexpensive and durable to prevent the need for frequent replacement of the electrolysis stack[13,14]. Various types of separators have been employed in alkaline water electrolysers, they include polysulfone, felt and woven forms of polytetrafluorethylene also known as Teflon, Polyphenylene Sulfide , asbestos, asbestos coated with polysulfone and Zirfon , which is produced via the addition of Zirconium dioxide to a polysulfone matrix. It should be noted that the use of asbestos has been discontinued due to the health risks associated with its use. The most widely used membrane separators are Zirfon based[15,16].

Solid Oxide Electrolysis

Solid oxide electrolysers consist of two porous electrodes enclosing an electrolytic membrane. Two forms of conduction are involved in hydrogen production, electric conduction for the external circuit between the electrodes and ionic conduction for the internal circuit for the conduction of ions between the electrolyte and the electrodes. There are two variations of the solid oxide electrolyser, oxygen ion conducting which employ non-porous metal oxide electrolytes that are O^{2-} conducting and proton conducting solid oxide electrolysers which employ proton conductive electrolytes. figure 1 shows the difference in the working of the two types. In the case of the oxygen ion conducting type, steam or water is supplied to the fuel electrode side where it is separated into oxygen and hydrogen ions. Hence, to obtain pure hydrogen, it needs to be separated from the reactant. The oxygen ions travel through the electrolyte to the oxygen electrode where they combine producing pure oxygen and electrons. While in the case of the proton conducting type, steam or water is supplied to the oxygen electrode side where it separates into oxygen, electrons and hydrogen protons. The protons travel through the electrolyte to the fuel electrode where they combine with electrons to produce hydrogen[17,18].

It is notable that in the proton conducting solid oxide electrolysers there is no requirement for hydrogen purification since it is produced at the fuel electrode which is inaccessible to the water supplied at the oxygen electrode since the electrolyte is impermeable to all other ions apart from protons. Additionally, their electrolytes become conductive at temperatures as low as 450 °C unlike the oxygen ion conducting type in which the electrolyte has limiting ionic conductivity even at 600 °C, hence having a comparatively lower efficiency[19].

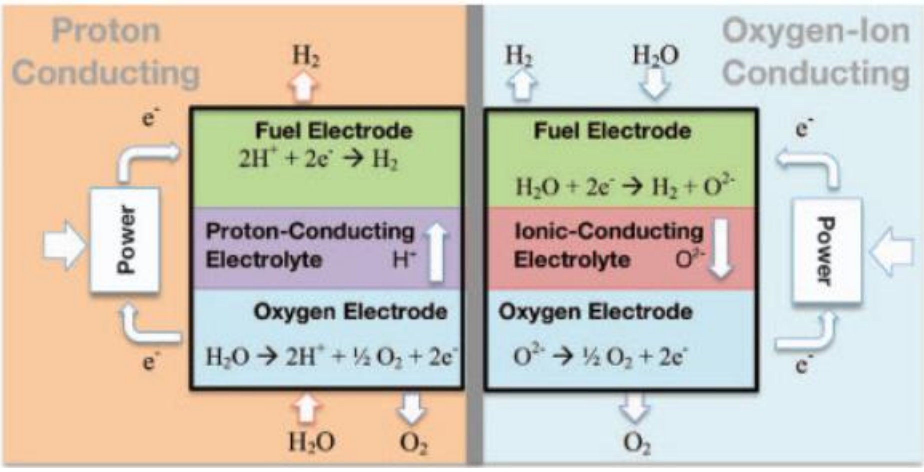

figure 1 depiction of the working of proton conducting and oxygen ion conducting SOECS [18]

The electrolytes are usually fabricated from materials that operate with minimal electrical conductivity at operating temperatures to avoid losses due to short circuiting. They must have adequately high ionic conductivities and they need to be stable in oxidizing and reducing conditions. The conductivity is dependent on the electrolyte material, operating temperature and design.

The most researched electrolyte for high temperature fuel cells is Yttria-Stabilized Zirconia (YSZ), due to its availability, chemical stability and non-toxicity, they have been the preferred electrolyte for oxygen ion conduction in solid oxide fuel cells since the onset. Therefore, utilised in solid oxide oxygen ion conducting water electrolysers too. However, it has low ionic conductivity at low temperature compelling the use of different materials. They include scandia-stabilized zirconia, Samaria-doped ceria, gadolinia-doped ceria, lanthanum strontium gadolinium manganite and lanthanum strontium gadolinium manganite cobaltite[20–26]. For proton conducting solid oxide electrolysers, the electrolytes employed include Barium Zirconium Yttria, Barium Cerium Yttria, Barium zirconate cerates, Barium zirconate and barium ceria yttria zirconate[27,28].

Proton Exchange Membrane Electrolysis

Proton exchange membrane electrolysers require membrane based electrolysers. In contrast with alkaline electrolysers that use aqueous solutions as their electrolytes, proton exchange membrane electrolysers have electrolytes that comprise thin, solid ion conducting membranes. In addition to hydrogen ion transportation from the anode to the cathode, the membranes also separate the hydrogen and oxygen gases produced. The merit of proton exchange membrane electrolysers over alkaline electrolysers is the relative safety and durability since the electrolytes employed are not caustic in nature. Additionally, the thin solid membrane facilitate comparatively faster ion transportation[29,30].

A breakthrough in polymer materials based on perfluorinated sulphonated acids unlocked new horizons in the production of proton exchange membranes due to their high chemical and mechanical stabilities and proton conductivities hence enabling zero gap arrangements in cell designs. They include Nafion by DuPont, Aciplex by Asahi Kasei, and Flemion by Asahi Glass as well as non-fluorinated such as sulfonated poly arylene ether ketone (S-PEEK) and Sulfonated Polyether Sulfone (S-PES). The membranes can be modified by fortifying the materials to increase their strength and durability. They are termed as reinforced perfluorinated sulphonated acids or fluorinated membranes. The most recognized reinforced perfluorinated sulphonated acids is Gore-Select, it is coated with polytetrafluoroethylene[31].

Alkaline Anionic Exchange Membrane Water Electrolysers

It is possible to create inexpensive electrolysers with elevated current densities and efficiency by combining the advantages of Proton exchange membrane electrolysis with alkaline electrolysis. This is because, although alkaline environments give the considerable benefit of employing economical and plentiful metals for catalysts and other cell components, Proton exchange membrane electrolysers offers high-performing water splitting cells at the expense of capital costs[32]. Therefore, a hybrid that employs the zero-gap design of Proton exchange membrane electrolysers and the merits of alkaline water electrolysers is the alkaline anionic exchange membrane water electrolyser. The main distinction between Proton exchange membrane and anionic exchange membrane is that conducted ionic species in the former are hydrated protons while the one in the latter are hydrated hydroxide ions[33,34].

As stated in the name, the membranes in alkaline anionic exchange membrane water electrolysers conduct anions. The membranes are made from anion-exchange polymers consisting of cationic headgroups attached to the polymeric backbones. The polymeric backbones could be either aliphatic or aromatic. The aliphatic backbones include Polyvinyl alcohol (PVA), Polytetrafluoroethylene (PTFE) also known as Teflon, Polyethylene-co-tetrafluoroethylene (ETFE) and Chitosan (CS). The aromatic backbones include Polysulfone (PSU/PSF) also known as Poly arylene ether sulfone, Polyether sulfone (PES) also known as Polyphenylene ether sulfone, Polyether ether ketone (PEEK), Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) also known as Poly (phenylene ether) (PPE). The attached functional group could be any of the following: Quaternary Ammonium, Imidazolium, Guanidinium, Phosphonium, Pyridinium and Sulfonium[35–37].

CONCLUSION

All types of water electrolysers require membranes to function properly. The role of the membrane could solely be gas separation like in the case of the alkaline water electrolysers or include the additional function of ion conduction from one electrode to another like in the case of solid oxide, proton exchange membrane and alkaline anion exchange membrane water electrolysers.

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