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Investigating Sustainable Materials for AEM Electrolysers: Strategies to Improve the Cost and Environmental Impact

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Abstract. In recent years, the EU policy identified the hydrogen as one of the main energy vectors to support the power production from renewable sources. Coherently, electrolysis is suitable to convert energy in hydrogen with no carbon emission and high purity level. Among the electrolysis technologies, the anion exchange membrane (AEM) seems to be promising for the performance and the development potential at relatively high cost. In the present work, AEM electrolysers, and their technological bottlenecks, have been investigated, in comparison with other electrolysers' technology such as alkaline water electrolysis and proton exchange membranes. Major efforts and improvements are investigated about innovative materials design and the corresponding novel approach as main focus of the present review. In particular, this work evaluated new materials design studies, to enhance membrane resistance due to working cycles at temperatures close to 80 °C in alkaline environment, avoiding the employment of toxic and expensive compounds, such as fluorinated polymers. Different strategies have been explored, as tailored membranes could be designed as, for example, the inclusion of inorganic nanoparticles or the employment of not-fluorinated copolymers could improve membranes resistance and limit their environmental impact and cost. The comparison among materials' membrane is actually limited by differences in the environmental conditions in which tests have been conducted, thereafter, this work aims to derive reliable information useful to improve the AEM cell efficiency among long-term working periods.

1 Introduction

After many years of hydrogen-oriented policy, the European Commission finally produced a report in 2020 as a communication directed to the European Parliament, the Council, the European economic and social committee and the committee of the regions [1] to state the urgency to build a strong clean hydrogen network as a key priority in the UE pathway towards a complete EU carbon neutrality in 2050 to implement the Paris Agreement, otherwise hard to reach [2]. This is just one of the last steps of the EU policy to accelerate the development of clean hydrogen as a carrier to guarantee an easy availability, transport and storage of the energy. Together with similar decisions made by other Countries, these policies could lead quickly to a breakthrough in the clean hydrogen production while, nowadays, the hydrogen production originates mainly from the steam reforming of fossil fuels, in particular of natural gas (via steam methane reforming) but also coal and oil [3]. Furthermore, the strategic importance of hydrogen is due to be a carbon-free and versatile tool with no dependency from any particular country; hydrogen is well-fitted to be coupled with renewable energy sources (RES) as an energy carrier and for energy storage purpose or converted in the form of chemicals as ammonia or methanol [4]. Hydrogen is also a candidate to replace fossil fuels in the industrial processes where a large amount of heat is required and allows accessing to a high efficiency technology such as the Fuel Cell, characterized by clean emissions and simultaneous production of electric current, heat (available for cogeneration in the high temperature fuel cell) and pure water.

Electrolysis includes a series of technologies able to produce hydrogen via electrochemical methods by means of electricity to split (relatively) pure water in oxygen and hydrogen. To obtain clean hydrogen, the required energy to feed the electrolysis should originate from clean sources, such as RES. Certainly, the clean target requirement makes electrolysis expensive and still not competitive with the fossil fuel-based technologies [5].

The EU is the leader in electrolyser capacity deployment with 40% of the global installed capacity, composed mainly by alkaline water electrolyser (AWE, 60%) and proton exchange membranes electrolyser (PEM, 31%) [3]. Solid oxide electrolysis cells (SOECs) and anion exchange membranes (AEMs) are new electrolyser technologies still emerging, so they do not really affect the overall hydrogen production; in particular, SOEC has outstanding features but is still a relatively immature technology, compared to the others, and because of this it will be omitted hereinafter. Between these electrolysis technologies, AEM seems particularly worthy of notice: compared to AWE, AEM exhibits a good dynamic operation behaviour, feature required when the electrolyser is coupled with RES, thanks to thin non-porous membrane that reduces significantly the crossover, main responsible for the slow AWE dynamics [6]. AEM avoids the typical AWE issues and shows the potential to combine the PEM pros (thin membrane, dynamic operation) and AWE pros (non-noble metal catalyst) [7] although durability and current densities are still far lower than showed from AWE and PEM respectively [8].

This paper aims to critically analyse the actual drawbacks in AEM technology compared with AWE and PEM, mainly related to membrane design, in order to find possible pathways for AEM optimization. In particular, membranes' geometry, materials and their interaction with other electrolysers' components will be taken in account.

2 Electrolysis Technologies

2.1 AWEs

AWE is a well-established technology with the extra value of non-adopting noble metal for the catalyst, making them a relatively cheap technology, although very energy demanding [9], and having a long lifetime (also beyond 100,000 hours) [10]. These devices are by far the most used in industry for hydrogen production [11]. The alkaline electrolysis principle is based on the application of electricity to a couple of electrodes, commonly in nickel [12] with an electrocatalytic coating, usually submerged in an electrolyte composed by a solution of potassium hydroxide (KOH) or sodium hydroxide (NaOH) dissolved in water [13]. A high alkaline concentration (typically, 25-30%) is mandatory to improve the electrolyte conductivity and then to reduce the transport losses [14]. In order to separate ions and gases (i.e. hydrogen and oxygen), anode and cathode are divided by a membrane/diaphragm [15] that also aims at conducting the hydroxide ion. Historically, the diaphragm is in asbestos but nowadays is forbidden in most countries, due to its toxicity leading to asbestosis and cancer [11]; more recently, it is made in Zirfon$^{\text{Ò}}$ or based on polymeric polysulfone binder [16]. AWE works between 25 °C and 100 °C and from 1 to 30 Bar of pressure [17], reaching a hydrogen production purity of 99% and efficiency up to 80% [11].

Hydrogen is produced by splitting the water at the cathode side, via Heyrovsky or Tafel reactions [18], together with the hydroxide ion, which carries the charge across the membrane; the hydroxide then moves to the anode side to discharge and be converted to oxygen [19].

This technology has some historical limitations such as the poor dynamic behaviour, from which arises low load flexibility (due mainly to the oxygen crossover towards the cathode), and as the high ohmic losses due to the diaphragm thickness [6] that implicates low current densities (below 0.4 A/cm^2 [8]) and efficiency loss; these issues make still challenging the AWE coupling with the (fluctuating) RES, without any further progress [20]. It follows that AWEs are designed for fixed processes at fixed operating conditions [21]. The needed purity level of water could also be an issue [19].

In the last decade, the efforts towards the so-called “zero-gap technology” are of particular interest: putting the electrodes adjacent the separator allows reducing the ohmic loss, leading to higher current densities [22]. It should be remembered that the hydrogen production is proportional to the current and working with high current is attractive because it allows to produce more hydrogen, keeping constant the capital costs.

2.2 PEMs

The membrane that characterizes the PEM electrolysers, usually in Nafion$^{\text{Ò}}$, provides high proton conductivity, low crossover and a thickness from 20 to 300 mm [10]. The membrane electrode assembly (MEA) is the heart of this technology and includes the membrane sandwiches between the catalyst layers (where the electrochemical reactions take place) and the gas diffusion layers in a tight sequence at the base of the compact system design [23]. In PEMs, the water splits electrochemically in oxygen and protons at the anode by producing two electrons collected by the electrode and then, the protons moved towards the cathode through the membrane that separated the anode side from the cathode side. At the cathodes, the protons reacquire the electrons to produce molecular hydrogen.

The PEM electrolysis is based on noble metal electrocatalyst at the electrodes, by means of materials such as Ir or Ru, in the form of oxides IrO_2 and RuO_2, at the anode (where the hydrogen evolution reaction, HER, occurs) and Pt/Pd at the cathode (where the oxygen evolution reaction, OER, occurs) [24]. The enhancement of the activity of the electrocatalysts toward the HER and the OER is one of the main topic of the current research on PEM [25].

PEM electrolysis is also characterized by high pure hydrogen production level [26], high current density (above 2 A/cm^2 but an operating current of 1 A/cm^2 is a common good practice), high efficiency, fast response (easy to couple to RES) and low operating temperature (20-80 °C) [27].

The drawbacks of this technology are the shorter lifespan and expensive materials (1,750 \$/kW) compared to the alkaline [3]. From the investment cost point of view, PEM is currently significantly more expensive than AWE (2,000 \$/kW_e vs. 1,400 \$/kW_e of capital expenditure, CAPEX, with no additional integration system equipment) but with a quicker cost reduction trend with the prospect to match the kW_e cost (500 \$/kW_e) in the next future [28]. Furthermore, the same Nafion$^{\text{Ò}}$ is expensive and is affected by some technical drawbacks, as the hydrogen crossover and poor stability at high temperature, so that new materials for membrane are investigated to lower the cost and improve the thermal and mechanical properties while maintaining the proton conductivity [29], as the hydrocarbon-based polymers [30], in particular, the cross-linked membrane type [31], or the radiation-grafted membranes [32].

2.3 AEMs

Anion-exchange membranes electrolysers have been drawing extensive academic and industrial attention as they do not employ rare and expensive metals for catalysts as well as expensive membranes with respect to PEMs [33], [34]. An AEMs system generally consists of an alkaline AEM membrane, non-noble metal electrocatalysts for both the anode and the cathode, and K_2CO_3 as electrolyte to provide the ionic conductivity [35]. An optimum current density of 500 mA/cm^2 is achieved at 1.9 V, on the other hand PEMs can operate at a current density of 2000 mA/cm^2 at about 2.1 V at 90 °C [35]. In comparison with PEMs, AEMs offers many benefits such like (i) free of leakage, (ii) simple utilization, (iii) compactness, (iv) reduced size and weight, and (v) simpler Balance of Plant [36]. However, much effort must be paid to their development to improve their performances with respect to efficiency and membrane lifetime. The substantial majority of the available data suggest that PEMs are capable to reach 10,000 h and above of lifetime, on the other hand, AEMs lifetime is limited to few hundred hours [37]. For first, due to a not optimized membranes’ thickness and morphology, ion transportation through the porous layer can be limited, negatively influencing the device performances. In addition, high working temperatures (50 °C and above) limit ionomer and membrane stability [38]. In order to fulfil the needed requirements, tremendous efforts have been devoted to designing new AEMs [39]. Furthermore, even considering totally commercial components, such as membranes or electrodes, a comparison of them is challenging due to different experimental conditions proposed as many variables can affect AEMs performance, such as, membrane pre-treatment method, gas diffusion layer (GDL) preparation and pre-treatment, assembly technique, etc. [40], [41].

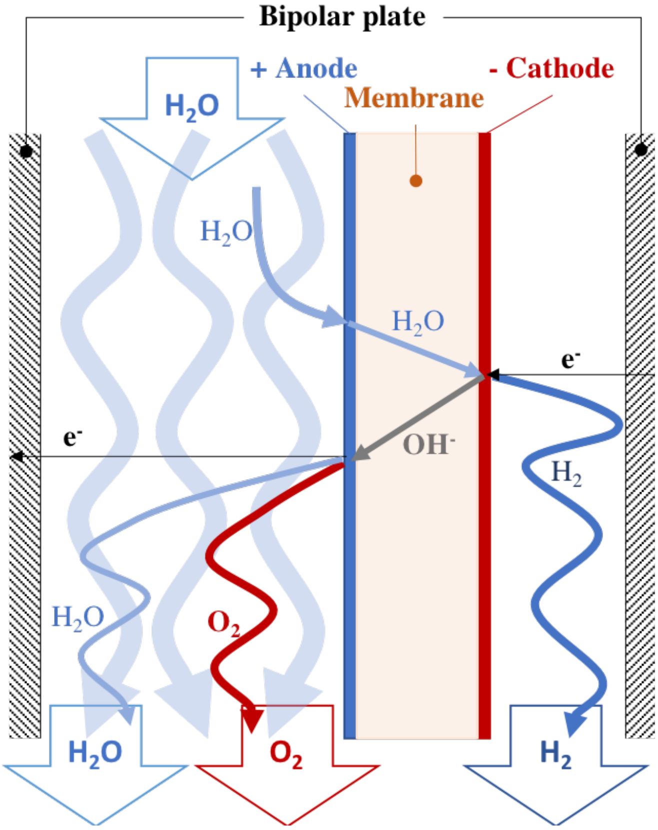

Figure 1. AEM scheme.

Table 1. Main Pro and Cons of the evaluated technologies [12],[13],[17].

	AWE	PEM	AEM
Pro	– Mature technology – Low-cost catalysts materials – Up to 150 MW – Suitable for long duration operation	– High performance – High voltage efficiency – Quick response – Compact size	– Catalysts with non-noble metals – Compact size – Suitable for small scale system – High pressure operating conditions
Cons	– Low current density – Corrosive electrolyte – Low pressure operating conditions – Electrolyte leakage	– Early market – Expensive components and materials – Corrosive electrolyte – Up to 0.5 MW	– Technology readiness – Low current density – Durability – Membrane degradation

3 Geometry

Regarding membranes' geometry, two main factors should be taken in account: dimensions, in particular thickness, and morphology, in terms of pore distribution and average diameter. These two factors, dimension, and morphology, affect directly the thermo-mechanical stability of AEMs, as well as their efficiency, and they can be adjusted for different potential applications. For example, thin membranes offer high conductivity for the transport of hydroxyl ions and are required for application in which high current densities and high pressure are needed [42].

AEMs' membranes show generally thickness in the range 10-50 μm, in contrast with thinner PEMs' membranes (180 μm) [34]. Despite the fact that AEMs ensures a shorter ion transfer pathway, as hydroxyl ion transport is slower than proton transport, AEMs still demonstrate lower ionic conductivity with respect to PEMs [43]. In addition, despite a lower AEMs thickness appears to be suitable to promote OH^-transfer and limit mass transport resistance, the operating conditions such as electrolyte concentration and working temperature (50 °C and above) can promote the membrane's physical damaging, thereafter, significantly modifying the overall electrolyser performance [34]. In particular, a relative elevated temperature is capable to promote a faster membrane degradation (holes are formed in membranes when the electrolyser cell is subjected to tightening) and this effect in particular thinner membranes [44]. In this sense, one of the most important works has shown the employment of an ultra-thin 9 μm membrane (A-901 – Tokuyama Corp.) in comparison with a conventional membrane (A-201 – Tokuyama Corp.) [35]. This work demonstrated that the best performance is achieved thanks to the employment of A-901 reaching 400 mA/cm^2 at 50 °C with a cell potential of 1.94 V, thereafter, showing slightly higher performance than the conventional A-201 membrane (around 1.80 V in the same condition). In addition, an improved stability of the A-901 was observed due to the higher water uptake with respect to A-201, indicating that the ultra-thin membrane is a suitable candidate for reducing the operational costs of electrolysis.

Regarding membranes' morphology has been demonstrated that a comb-like architecture should be preferred as it promote the formation of hydrophobic/hydrophilic micro-phase separation, with several beneficial aspects: (i) interconnected hydrophilic channels are capable to act as favourable path for ion conductivity; (ii) degradation of the hydrophobic phases due to physical contact with the hydrophilic one, is limited [45]. In this sense, polymers with this type of morphology should be preferred such as modified quaternary ammonium groups (QAs) and commercial, but expensive, compounds, such as Nafion®.

4 Materials

From a chemical point of view, AEMs working principle is based on negative ions transport (OH^-, Cl^{2-}, etc.), thereafter, this mechanism is obtained through the presence in the membrane's polymer backbone of positive functional group that are capable to organize preferred pathways for negative ions transport. The most employed material is based on benzyl-type quaternary ammonium groups (QAs) due to its ease of preparation and relative high stability, but it can hardly meet the long-term stability under alkaline operational conditions [46], [47]. In fact, its main drawback is due to high nucleophilic attachment of hydroxyl groups to the QA groups that significantly decrease the termo-mechanical stability of the polymer backbone, as well as the ionic conductivity of the overall system [48]. This condition occurs when high temperature (above 50 °C) or high pH (above 12) are employed. For this reason, different strategies have been proposed in order to improve material's stability and the most studied is the partial substitution of QAs with organic and inorganic compounds, such as: polyphenylene oxide [49], poly-arylene ether ketone [50] poly-ether ether ketone [51], titanium dioxide (TiO2) [52], aluminium oxide (α-Al2O3) [53], bentonite [54] and graphene oxide [55].

Taking to account organic functionalization, that is the most employed strategy, different mechanism are exploited: poly(arylene ether)s, such as poly phenylene oxide, poly ether ketones, and poly ether sulfones are well known to resist to an elevated pH environment, as they exhibit less suppression of the hydrogen adsorption-desorption features, as well as less hindrance towards the oxygen reduction reaction. A recent article demonstrated substantial improvement by employing a quaternary ammonium grafted polyvinyl benzyl chloride membrane, as a current density of 100 mA/cm^2 was obtained at 1.99 V and 55 °C, due to the overall increasing mechanical resistance of the tested material with respect to QAs [56]. In strong similarity, Wu et al. have reported the experimental results of the employment of a polymethacrylate-based quaternary ammonium, which shown a performance of 100 mA/cm^2 at 1.9 V [36]. Other studies demonstrated a similar effect due to chitosan and carbon nano-tubes addition, as an enhancement of membrane tensile strength and chemical stability has been observed by increasing the carbon-nanotube amount [57]–[60]. Nevertheless, a reduction of the OH group conductivity of about 15 mS/cm was observed. More promising results have been obtained by employing functionalized graphene oxide, as it is capable to interpenetrate the membrane's polymer network [61]. In this case, not only an improvement of the termo-mechanical stability of the membrane was achieved but also an enhancement of the OH conductivity (12.1 mS/cm 30 °C and 21 mS/cm at 80 °C), in comparison with the bare membrane (7.14 at 30 °C and 9.04 mS/cm at 50 °C). Other investigated groups are: pyridinium [62], imidazolium [63], guanidinium [64], quaternary phosphonium [65] and tertiary sulfonium [66] but limited data existed for a reliable comparison of the stability of all these cation groups.

Concerning commercial materials, a complete review indicates that generally research-based membranes outperform the great majority of the commercial materials, due to the fact that all materials that are included in the electrolyser cells (membrane, ionomer, catalyst, cell design etc.) need to be optimized together [67]. For the same reason, it is quite difficult to rank commercial materials for membrane, even if Aemion and Sustanion membrane shows in general higher ion conductivity with respect to Fumasept or A201 [67]. Nevertheless, more investigation is needed for lifetime and performance estimation in particular working environment, such as above 50 °C and above pH = 12. Regarding the functionalization of commercial materials, one of the most promising studies is related to Fumion FAA-3-SOLUT-10 ionomer (Fumatech) mixed with graphene in different concentrations [68], [69]. The best result (conductivity of 113.27 mS/cm at 80 °C) was achieved by employing 0.50 wt% of graphene, as a further addition of graphene (0.75 wt% and 1 wt%) occurred in a deceasing of OH conductivity, probably due to the disruption of the hydroxide transport pathways through the composite-membranes. In addition, it has been demonstrated that graphene increases the membrane stiffness as well as the thermal stability when compare with commercial FAA3-20 and FAA3-30. Regarding the economic potential benefit of sustainable materials such as chitosan, among commercial membrane it must be underlined that FAA3 (Fumatech) quotation is actually 14.9 \$/g and this is one of the more economic commercial materials, whereas pure chitosan is quoted 2.5 \$/g [67]-[70]-[71].

5 Interaction with Other Electrolysers' Components

Several studies demonstrated that hydroxide containing polymers show the highest performance (399 mA/cm^2 at 1.8 V and 50 °C) as membrane for electrolysers in aqueous alkali environment due to the fact that the highest chemical compatibility among OH$^-$ group and water is achieved, thereafter, promoting the transport mechanism [72]–[74]. Nevertheless, alkaline environment is well-known to strongly interact not only with AEM membranes but also with their auxiliary equipment in all the electrolyser cell and electrodes due to corrosion, which could be further promoted by elevated temperatures (above 50 °C) [42]. Thereafter, performance improvement in such environment could be achieved by promoting membrane conductivity or its interface with electrode assemblies [72]. Nevertheless, an increasing AEM conductivity is generally associated with lower mechanical stability and higher water uptake in particular for thin membranes, thereafter, more research is needed in that sense [33], [35].

In addition, it has been demonstrated that the employment of not-noble metals as electrodes, such as Ni, Fe, Co is a favourable condition for AEMs with respect to PEM as similar performance after 1,000 h can be obtained (1 A/cm^2 at about 1.9 V) without employing high-cost metals [73], [75]. In addition, it has been demonstrated that coupling not-noble metals with the catalyst-coated membrane approach, a further improvement in performance can be achieved (6 A/cm^2 at 2.05 V) [75].

6 Conclusions

Nowadays, AWE, PEM and AEM are leading technologies in the electrolysis applications for clean hydrogen production. In this paper, these technologies are first described in the main operating principles and then compared each other to highlight pros and cons of each one. In particular, AWE emerges for readiness and cost-effectiveness although with a slow dynamics that makes it best suited for static industrial operation. PEM is still an expensive technology in spite of the hard efforts in materials research to lower the costs and to improve the thermal and mechanical stability; on the other side, the fast dynamics together with other features (high current density, high efficiency) makes PEM the ideal electrolyser to couple with RES. Finally, AEM is a halfway technology considerably cheaper than PEM but with still good dynamic behaviour, among other features. Actually, the strong point of AEM is the materials' development potential that shows a good room for growth, in particular in the membrane research.

In this paper, the performance of various membranes for AEMs electrolysers has been compared to determine possible route of improvement, in order to promote AEMs technology with respect to other such as PEM. The main result achieved in this study is that tailor made, and functionalized membranes show high potential with respect to commercial materials, due to the strong interaction with the other materials composing in the electrolyser cell (electrodes, catalysis, etc.). In addition, further studies must be dedicated to exploit electrolyser performance in extreme working condition such as pH above 12 and temperature above 50 °C to improve membrane lifetime.

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