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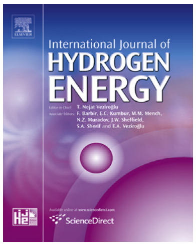

Stand-alone operation of an alkaline water electrolyser fed by wind and photovoltaic systems

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ABSTRACT

Over the last few years, hydrogen technologies have established themselves as key enablers in the medium and long-term development of a new energy model that offers greater sustainability and independence than the present-day one. In this respect, the integration of water electrolysis with renewable energy-based systems can play an important part in the large-scale production of sustainable hydrogen. This paper reports on the complete experimental characterisation of a 1 Nm^3 h^{-1} alkaline water electrolyser located in the Public University of Navarre (UPNa). Specifically, a study was made of the electrical performance, hydrogen production rate, purity of the gases generated and energy efficiency, for a range of operating currents (40–120 A), temperatures (35–65 °C) and pressures (5–25 bar). Additionally, an experimental study was conducted on the electrolyser operation under conditions that are characteristic of a stand-alone wind power and PV-based renewable energy system, installed at the UPNa. The results obtained for the wind power and PV emulations showed that the electrolyser performed correctly, with regard to balance of plant and its principal electrochemical characteristics. Furthermore, the mean energy efficiency of the electrolyser was 77.7% for the wind power emulation, and 78.6% for the PV emulation on a day with stable irradiance, and 78.1% on a day with highly variable irradiance (day with scattered clouds).

1. Introduction

Hydrogen can be stored, transported and used in a wide range of applications in which fossil fuels are currently used [1–8]. However, hydrogen is not a source of energy in itself, but an energy carrier that must be obtained by industrial and technological methods, given the fact that it is not found in a free natural state. From a sustainable point of view, the synergy existing between hydrogen and renewable energy sources is of particular interest. Although a number of methods are available for the production of hydrogen from renewable sources, water electrolysis is currently the best method available [9–11].

There are basically three types of hydrogen-producing electrolysers, depending on the type of electrolyte used: alkaline; solid polymer; and solid oxide [11]. Regardless of the technology, the overall electrolysis reaction is the same:

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad (1)$$

The electrolysis reaction in standard conditions (298.15 K and 1 atm) provides a reversible voltage (V_{rev}) of 1.229 V and a thermoneutral voltage (V_{tn}) of 1.481 V [11].

Today, alkaline electrolysers are the most well-established and marketed technology, given their good technical

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performance and economic benefits. The main alkaline electrolyser manufacturers have opted for the zero-gap bipolar configuration directed at optimising energy consumption [11–16]. These devices have an average useful life of between 10 and 20 years with a cost ranging from 5000 to 25,000 € per $Nm^3\ h^{-1}$ based on the electrolyser production capacity [17,18]. Over the last few years, considerable progress has been made in alkaline electrolysis, seeking to improve the performance of the electrolysis system in order to minimise the costs of the electricity consumed and also to increase the electric current density with a view to reducing the capital investment costs [11,19]. Larger units can reach a hydrogen production rate of 760 $Nm^3\ h^{-1}$, with a current density of around 0.4 A cm^{-2} and an electricity consumption of some 3530 kW. The minimum alkaline electrolyser hydrogen production level is around 25–40% of its rated capacity. This lower operating limit is intended to prevent the formation of potentially flammable mixtures of hydrogen and oxygen caused by the high diffusional flux of these gases through the diaphragms at low charge levels. The permitted operating temperature for these electrolysers is from 5 to 100 °C, whilst the operating pressure may vary from atmospheric pressure, when using atmospheric electrolysers, up to some 10–30 bar when using pressurised electrolysers. Furthermore, the purity of the hydrogen and oxygen produced can be as high as 99.9 vol.% and 99.7 vol.%, respectively, without any auxiliary purification equipment. In turn, the water used in the alkaline electrolysis process must meet some minimum purity requirements, generally involving a conductivity of less than 5 $\mu S\ cm^{-1}$. The electrolyser requires demineralised water in order to guarantee a high durability of the module components, to minimise corrosion problems and undesired electrochemical reactions, and to maximise process efficiency.

The alkaline electrolysis cells making up the stack comprise two electrodes, the anode and cathode, separated by a diaphragm. These electrodes are immersed in an electrolyte fluid which is generally an aqueous solution of potassium hydroxide (KOH) with a concentration of 25–30 wt.% to maximise the ionic conductivity of the electrolyte for the normal operating temperature range (65–90 °C). During the electrolysis process, the direct current flowing between the electrodes causes the water molecules to dissociate into hydrogen and oxygen. The reduction half-reactions take place at the cathode based on Eq. (2), where the water is reduced to release hydrogen and hydroxide ions (OH^-). The hydrogen leaves the cathode compartments and rises to the surface, whilst the electrical field made by the power supply causes the hydroxide ions to migrate to the anode through the diaphragm. In turn, the oxidation half-reactions occur at the anode, based on Eq. (3), where the hydroxide ions are oxidised to oxygen and water. The oxygen leaves its compartment and rises to the surface, and the water returns to the solution:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq.) \tag{2}$$

$$2OH^-(aq.) \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^- \tag{3}$$

At a global level, there are currently few manufacturers developing solid polymer electrolysers, basically due to the high cost involved (50,000–100,000 € per $Nm^3\ h^{-1}$), limited useful life (relative low durability of the membrane electrode assemblies) and limited hydrogen production capacity (10–30 $Nm^3\ h^{-1}$) compared to alkaline electrolysers [11,20–23]. Nevertheless, solid polymer electrolysers offer considerable scope for improvement in order to compete with and complement alkaline electrolysers in the not-to-distant future. This electrolyser technology, termed proton exchange membrane (PEM), uses an electrolyte formed by a solid polymer membrane with a strongly acidic character due to the presence of functional groups of sulfonic acid ($-SO_3H$) which perform the proton exchange (H^+) and therefore the charge transfer through the membrane. The PEM electrolysis modules are series coupled through bipolar plates, electrically connecting the cells and also helping to channel and remove the gases generated during the process. The oxidation half-reactions take place at the cell anodes where the water molecules oxidise according to Eq. (4) to give oxygen and protons. The electrical potential created by the external power source causes the protons migrate to the cathode through the electrolyte. Likewise the reduction half-reactions take place at the cathodes, where the protons capture electrons to form hydrogen, based on Eq. (5):

$$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq.) + 2e^- \tag{4}$$

$$2H^+(aq.) + 2e^- \rightarrow H_2(g) \tag{5}$$

Solid oxide electrolyte (SOE) electrolysers are still at the R&D stage [11]. This electrolyser technology operates at high temperatures in the 600–1000 °C range, and therefore electrolysis takes place in the form of steam. The high operating temperatures considerably reduce process electricity consumption. SOE electrolysers show great potential in certain applications in which high temperature power supplies are available to cover the thermal requirements of the process (for example the thermal power plant cooling circuits). The SOE cells can be one of two configurations. Either planar cells, with a similar arrangement to that of a PEM electrolyser, or tubular cells, where the cathode electrode is located in the cylinder interior and the anode on the exterior [24–26]. SOE electrolysers use a solid ceramic electrolyte (generally yttria-stabilised zirconia) which conducts the oxide anions (O^{2-}) through the membrane when subjected to temperatures of more than 600 °C. The reduction half-reactions take place at the cathodes, according to Eq. (6), where the steam is reduced to give rise to hydrogen and oxide anions. These ions are transported through the membrane to the anode, where they are oxidised to give oxygen, in accordance with the oxidation half-reaction shown in Eq. (7):

$$H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \tag{6}$$

$$O^{2-} \rightarrow \frac{1}{2}O_2(g) + 2e^- \tag{7}$$

Based on this analysis of the current status of the electrolysis technologies, it can be seen that the alkaline electrolyser is the most highly developed and is, therefore, the best one for the production of hydrogen from renewable energies. In turn, the wind and PV energies are the best positioned for integration with electrolysers, given the spectacular development of