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HAZOP study of a water electrolysis plant used in green hydrogen production

Farhana Yasmine Tuhi

Department of mechanical and industrial engineering, Norwegian university of science and technology (NTNU), Norway. E-mail: farhana.tuhi@ntnu.no

Marta Bucelli

Gas technology, SINTEF energy research, Norway. E-mail: marta.bucelli@sintef.no

Yiliu Liu

Department of mechanical and industrial engineering, Norwegian university of science and technology (NTNU), Norway. E-mail: yiliu.liu@ntnu.no

To advance the green hydrogen economy, ensuring high reliability and safety of the water electrolysis plant is crucial. This study presents a HAZard and OPerability (HAZOP) analysis to identify the probable deviations in a water electrolysis plant with proton exchange membrane (PEM) electrolyzer from its intended operation, along with their causes and consequences. HAZOP is a risk and reliability analysis technique that identifies operational failures by analyzing logical sequences of cause-deviation-consequence for various process parameters. To conduct HAZOP, the water electrolysis plant is divided into sub-subsystems and deviations for each sub-systems is identified using guideword and process parameters. A literature review is performed to identify the causes and consequences of each deviation and recorded in a dedicated HAZOP table. The HAZOP analysis shows that deviations in a PEM electrolyzer are interconnected, with one deviation potentially triggering another. The performance of the entire plant is heavily influenced by its sub-systems, as faults in auxiliary components can impact the electrolyzer's efficiency, degradation, and safety. Key consequences of these deviations include reduced efficiency, degradation of the PEM electrolyzer, and the formation of a flammable mixture. This work provides great input for forecasting component failures and performing maintenance actions to prevent failures/ accidents, or to restore desired hydrogen production rate.

Keywords: Green hydrogen, HAZOP, water electrolysis, PEM electrolyzer, reliability.

1. Introduction

Green hydrogen, produced through water electrolysis using renewable energy sources like solar, wind, or hydro power, is gaining significant attention for its carbon-neutral production process. It holds potential for decarbonizing sectors such as transportation and hard-to-abate industries like aluminum, glass, and steel. Besides, its derivatives such as green ammonia and green methanol show promise as fuels for maritime and automotive applications, as well as for industrial heating. Additionally, green hydrogen serves as a bridge between renewable electricity and various end-use applications by enabling the storage, transportation, and distribution of renewable energy across different regions (Kang 2021). Currently, there are four available water electrolysis technologies for splitting water: alkaline water electrolysis, proton exchange membrane (PEM) water electrolysis, anion exchange membrane (AEM) water electrolysis, and solid oxide (SO) water electrolysis (Shiva Kumar and Lim 2022). The alkaline, PEM and AEM are low temperature electrolysis whereas SO is known as high temperature water electrolysis process. Besides, the alkaline and PEM electrolyzers are well-developed technologies used in industries, while AEM and SO electrolyzers are still in the research and development (R&D) phase (IRENA 2020). The technical characteristics of these technologies are summarized in Table 1. However, PEM electrolyzers, in particular, offer benefits such as higher energy efficiency, broader operating temperature ranges, and better adaptability to the intermittency of renewable energy sources than other available electrolyzers (Salehmin et al. 2022). Therefore, this study focuses on water splitting process using PEM electrolyzer only.

Though the electrolyzer is the main component for producing green hydrogen, a water electrolysis plant also includes various auxiliary components. Fig.1. illustrates a standard layout of a water electrolysis plant with a PEM electrolyzer. The plant draws power from renewable sources like wind, solar or hydro power to supply the required voltage and current density to conduct the water electrolysis reaction. Also, there is a water purification plant for removing impurities to produce water of ASTM type I or II quality since impurities can affect the lifetime and performance of the electrolyzer stack (Zeng and Zhang 2010). Water, charged from the anode side of the electrolyzer, is decomposed to generate oxygen and hydrogen. The generated oxygen is released to the atmosphere after oxygen/liquid separation process. The remaining hydrogen ions pass through the membrane to the cathode side where hydrogen gas is produced. The hydrogen undergoes hydrogen/liquid separation, deoxidization and drying process to remove moisture and any remaining oxygen. This process yields to hydrogen with 99.9-99.9999% purity. Finally, the resulting hydrogen is compressed and stored as compressed gaseous hydrogen. However, the specific properties such as, wide flammability range (4-75% in air by volume (Ono et al. 2007)), minimum ignition energy (0.017 mJ (McCarty 1981)) and high burning velocity unfolds several reliability and safety issues in the application of hydrogen. There exist several review articles (Abohamzeh et al. 2021; Moradi and Groth 2019; Najjar 2013) analyzing the probable consequences of hydrogen release and emphasizing the implementation of effective safety strategies across the hydrogen value chain. (Tuhi, Bucelli, and Liu 2024) analyzed previous accidents occurred in water electrolysis plant. Such failures caused hazardous consequences such as fire and explosion leading to human injuries and plant downtime. In another study, (Tuhi et al. 2024) highlighted that the failure events are often indicated by sudden changes in operating conditions and monitoring these conditions can help detect failures before accident occurs. Therefore, a comprehensive analysis must be performed to investigate operability problems along with their causes and consequences on the overall plant to ensure smooth operation and reduce financial losses.

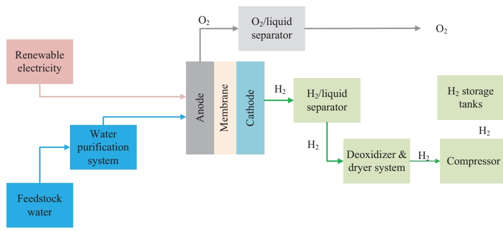

Fig. 1. Schematic of a water electrolysis plant involving PEM electrolyzer.

The HAZard and OPerability (HAZOP) is a well-developed risk and reliability analysis technique used to investigate how a system, or plant might deviate from its design intent, potentially causing safety and operability issues (Rausand and Haugen 2020). HAZOP has been successfully applied in the chemical and petroleum industries to obtain safer, more efficient, and more reliable system operations. In the context of green hydrogen production, two notable HAZOP studies exist. (Hadef et al. 2020) conducted a partial HAZOP analysis on a lab-scale alkaline electrolyzer used for hydrogen production. In total 33 failure scenarios were identified and categorized based on their probabilities and consequences. However, all the failure modes were not provided in the article. In another study, (Kasai et al. 2016) performed a hybrid HAZOP and failure mode and effect analysis (FMEA) on an electrolytic high pressure hydrogen gas generation system. In their analysis, they documented process deviations, trigger phenomena, and safety measures in a HAZOP result sheet but the article included details for only a single deviation. While these studies present process deviations for electrolyzer system, there are critical gaps in understanding the impact of deviations of auxiliary components, highlighted in (Tuhi, Bucelli, and Liu 2024).

Table 1. Technical characteristics of available water electrolysis technologies.

	PEM	Alkaline	AEM	Solid oxide
Operating temperature (°C)	50-80	70-90	40-60	700-850
Operating pressure (bar)	<70	1-30	<35	1
Current density (A/cm^2)	1-2	0.2-0.8	0.2-2	0.3-1
Voltage range (V)	1.4-2.5	1.4-3	1.4-2.0	1.0-1.5
Purity of produced H_2 (%)	99.9-99.9999	99.5-99.9998	99.9-99.9999	99.9
Water purity (ASTM)	Type I or II	Type I or II	Type I or II	Type I or II

In this work, a HAZOP analysis is conducted for a standard water electrolysis plant involving PEM water electrolyzer, aiming to identify potential deviations that could disrupt the plant's smooth operation and reliability. The results of this HAZOP study can be used to predict equipment failures based on changes in process parameters, understand the impact of intermittency of energy sources, and address operability issues affecting hydrogen production. Additionally, the findings can aid in conducting maintenance activities to prevent failures, and to restore desired hydrogen production rate or purity. Overall, this study contributes to the implementation of a highly safe and reliable water electrolysis plant to reinforce the green hydrogen economy. The article is structured as follows: the research methodology adopted in this study and the system description are described in Section 2. Section presents the results of the HAZOP analysis followed by a discussion in Section 4. Finally conclusions are presented in Section 5.

2. Method

The HAZOP involves a structured and systematic assessment of a planned or existing process/operation in order to identify and evaluate problems representing risks or preventing efficient operation. This was first developed by ICI Ltd in 1963 for the chemical industry (Rausand and Haugen 2020). The HAZOP approach assumes any operation problem that may arise in a system or equipment is the cause of the deviations from the normal operation of a process variable or parameter (Mocellin et al. 2022). Guidewords assist in forming hypothetical deviations related to the system. Table 2 presents standard guidewords and their generic meanings, adopted from HAZOP: Guide to Best Practice by IChemE (Crawley and Tyler 2015).

Examples of process parameters are flow, pressure, temperature, viscosity, and time. The guidewords and the process parameters should be combined in such a way that they lead to meaningful process deviations, hence, all the guidewords cannot be applied to all process parameters (Rausand and Haugen 2020). HAZOP analysis also investigates the causes and the results of the deviations. Finally, HAZOP study identifies safety barriers for reducing the frequency of the deviation or to mitigate its consequences. The main international standard for HAZOP is IEC 61882 (2016). Typically, HAZOP analysis is carried out by a group of experts, commonly known as HAZOP team, thus the quality of the study depends on the team's qualification.

The HAZOP analysis conducted in this work followed the procedure described in HAZOP: Guide to Best Practice by IChemE (Crawley and Tyler 2015). Fig. 2. illustrates the flow diagram adopted for performing HAZOP in this study. To perform HAZOP, the water electrolysis plant, presented in Fig. 1. is divided into sub-systems based on their functions and reference operational parameters are defined for each item by studying relevant literatures. To identify the deviations resulting in equipment failure, accident or reduced production, parameter-first approach is adopted. At first a parameter from each subsystem is taken and is combined with each guideword in turn to form a meaningful deviation. A specific set of guidewords (see Table 2) is used for this purpose. Furthermore, to investigate the causes and consequences of the identified deviations, a literature review is performed. Finally, all the deviations, causes and consequences are recorded in a dedicated HAZOP table. By performing the HAZOP analysis, the deviations in the operational parameters are identified which demonstrates under what conditions green hydrogen production is reduced, or even stopped. However, in this study the safeguards to mitigate the effects of the consequences are not studied. Also, risk assessment was not performed since this was outside the scope of the work.

Table 2. Standard guidewords and their generic meanings (Crawley and Tyler 2015).

Guideword	Meaning
No (not, none)	None of the design intent is achieved
More (more of, higher)	Quantitative increase in a parameter
Less (less of, lower)	Quantitative decrease in a parameter
As well as (more than)	An additional activity occurs
Reverse	Logical opposite of the design intention occurs
Other than (other)	Complete substitution

3. Result: HAZOP analysis

3.1. *Sub-system analysis*

The entire production plant, presented in Fig. 1., is divided into several subsystems based on their functions. The subsystem analysis of the plant along with selected process parameters for each subsystem is depicted in Fig. 3. Each of the sub-systems are described in the following part of this section.

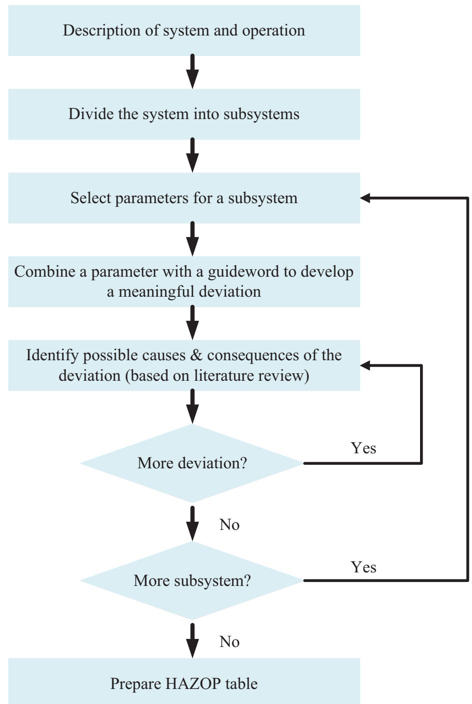

Fig. 2. Overall research methodology.

- **Energy source:** Renewable electricity is termed as energy source subsystem. The process parameter selected for this subsystem is power since this supplies the required energy required to perform the water electrolysis chemical reaction.
- **Water purification unit:** This subsystem includes feedstock water and the water purification plant. The main purpose of this unit is to provide pure water to the electrolyzer and hence, water purity is selected as the process parameter.
- **PEM electrolyzer:** The PEM electrolyzer is the core element of the plant. The operating conditions of the electrolyzer including water flow, cell voltage, current density, cell temperature and operating pressure are crucial for the proper functioning of an electrolyzer, hence, selected as the parameters. Typical working condition of a PEM electrolyzer is listed in Table 1.

- **Hydrogen processing unit:** The hydrogen/liquid separator, deoxidization and dryer system are grouped together as the H_2 processing unit which is responsible for maintaining purity of the produced hydrogen. Hence, hydrogen purity is considered as the parameter for this subsystem.
- **Oxygen processing unit:** This subsystem includes oxygen/liquid separator which processes produced oxygen.
- **Hydrogen storage**: This subsystem includes compressor and hydrogen storage tanks.

Both oxygen/liquid separator and H_2 storage is outside the system boundary (represented by the dotted line in Fig. 3.) therefore, not considered in the HAZOP analysis.

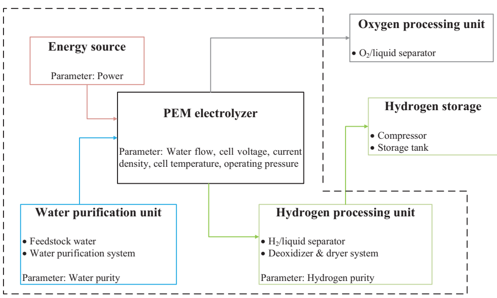

Fig. 3. Subsystem analysis of a water electrolysis plant.

3.2. *HAZOP analysis*

The guidewords selected for this study are more and lower. All the process parameters and associated guidewords are presented in Table 3. The combination of process parameters with these guidewords provides potential deviation such as, lower power, lower water purity, lower water flow, higher cell temperature and higher current density. The probable causes and consequences for each deviation is recorded in the HAZOP table, presented in Table 4. For example, first deviation reported in the table is 'lower water quality' which resulted from faults in the water purification system.

Due to this deviation, impurities enter the electrolyzer and can lead to degradation. In addition, this can result in higher capital expenditure (CAPEX) due to less durable electrolyzer. However, the cause recorded for this deviation is a generic one and this approach is followed for other deviations such as, lower power supply, lower water flow and lower hydrogen purity. On the other hand, detailed study on the causes and consequences of deviations related to electrolyzer operation such as lower cell voltage, lower current density, lower operating temperature, higher operating temperature, higher operating pressure, higher current density and higher cell voltage are presented due to the availability of extensive research work.

Table 3. Subsystem study for HAZOP analysis

Subsystem	Process parameter	Guideword
Energy source	Power	Lower
Water processing unit	Water purity	Lower
Electrolyzer system	Water flow	Lower
	Cell voltage	Lower, More
	Current density	Lower, More
	Cell temperature	More
	Operating pressure	More
	H_2 concentration in produced O_2	More
	O_2 concentration in produced H_2	More
H_2 processing unit	Hydrogen purity	Lower

4. Discussion

In this study, HAZOP analysis is conducted for a water electrolysis plant involving PEM electrolyzer. By using the HAZOP table, the causes and consequences of each deviation can be easily analyzed, facilitating the implementation of appropriate mitigation and prevention measures. The HAZOP analysis reveals that the recorded deviations for the PEM electrolyzer are interconnected, in other words, one deviation can trigger another. For example, higher current density may result in higher operating temperature and pressure. Furthermore, the reliable performance of the entire plant is significantly influenced by the performance of the sub-systems, as the electrolyzer's efficiency,

Table 4. Result of HAZOP analysis

Guide word	Deviation	Possible causes	Consequences
Less	Lower water quality	Fault in water purification system.	Degradation of electrolyzer (Zeng and Zhang 2010), Increase in CAPEX due to less durable electrolyzer (IRENA 2020).
	Lower power supply	Variability in renewable energy production.	No electrolysis reaction (Majumdar et al. 2023).
	Lower water flow	Fault in water flow system.	Formation of hotspots in electrolyzer membrane (Immerz et al. 2018), Decreased electrolyzer efficiency (specially at low current density) (Lee et al. 2019).
	Lower cell voltage	Insufficient power supply from the energy source. Electrical short circuit inside electrolyzer(Millet et al. 2012).	Decreased electrolyzer efficiency, No electrolysis reaction when falls below the threshold value (Khatib et al. 2019).
	Lower current density	Uncontrolled decrease in power supply (Majumdar et al. 2023).	Degradation of electrolyzer cell membrane (Chandesris et al. 2017), Increased hydrogen concentration in oxygen side (Trinke, Bensmann, and Hanke-Rauschenbach 2017).
	Lower operating temperature	Fault in water flow system (Majumdar et al. 2023).	Decreased electrolyzer efficiency (Lee et al. 2019).
	Lower H_2 purity	Fault in the H_2 processing unit.	Produced H_2 with lower purity level.
More	Higher operating temperature	Reduced water flow (Immerz et al. 2018), High current density (Trinke, Bensmann, and Hanke-Rauschenbach 2017)	Degradation of electrolyzer cell membrane (Lee et al. 2019), Increased H_2 concentration in O_2 side (at low current density) (Trinke, Bensmann, and Hanke-Rauschenbach 2017).
	Higher operating pressure	High current density (Sakai et al. 1985).	Increased cross permeation of H_2 & O_2 gases (Grigoriev et al. 2011), Increased operating voltage (Santarelli, Medina, and Calì 2009), Degradation of electrolyzer (Krenz et al. 2023).
	Higher current density	Uncontrolled increase in power supply since current is an input from the electricity source (IRENA 2020), Reduced membrane thickness (Majumdar et al. 2023)	Rapid bubble formation which covers the electrode area leading to hotspot formation (Majumdar et al. 2023), Increased H_2 concentration in O_2 side (observed at elevated cathode pressure) (Trinke, Bensmann, and Hanke-Rauschenbach 2017), Degradation of electrolyzer (IRENA 2020).
	Higher cell voltage	Mechanical failure due to corrosion and overheating(Sood et al. 2022), Degradation of electrolyzer due to aging (Majumdar et al. 2023).	Decreased electrolyzer efficiency (Lee et al. 2019).

degradation and safe operation are heavily dependent on the proper functioning of these auxiliary units. The causes listed in the HAZOP table clearly indicate that faults in auxiliary components and deviations from their intended operation can impact the electrolyzer's performance. For instance, a fault in the water flow system can reduce water flow inside the electrolyzer, leading to its degradation. Additionally, a fault in the hydrogen processing sub-system can result in hydrogen with lower purity levels, thereby affecting the overall reliability of the plant. The resulting consequences from all the deviations can be examined from three main perspectives: reduced efficiency, degradation of PEM electrolyzer, and the formation of flammable mixture.

- **Reduced efficiency:** According to the HAZOP study, if the cell voltage drops too low, the electrolyzer's efficiency may decrease, and hydrogen production can even stop. These events primarily result from the intermittent nature of the renewable sources. Moreover, the efficiency of a PEM electrolyzer is significantly affected by reduced water flow, particularly when the electrolyzer operates at a low current density. Additionally, the efficiency of the electrolyzer decreases when operating at lower temperature and higher cell voltage. Degradation due to aging or corrosion increases the cell voltage, thus decreasing the efficiency as more power is drawn to conduct the electrolysis process. The reduction in hydrogen gas purity is directly linked to inappropriate actions within the hydrogen processing unit which can compromise the overall reliability of the entire plant.
- **Degradation of PEM electrolyzer:** Based on the HAZOP results, deviations from the standard operating conditions cause degradation of the PEM electrolyzer. When low quality water enters the electrolyzer, impurities can corrode the electrodes, resulting in unexpected failure events. The HAZOP analysis attributes this issue to a fault in the water purification unit. Additionally, deviations such as lower current density, higher operating temperature, higher operating pressure and higher current density contribute to degradation of electrolyzer which results in reduced lifetime or sudden electrolyzer failure. The analysis also reveals that maintaining the current density within the standard range is very crucial for preventing degradation of the electrolyzer. Another important parameter is the water flow inside the electrolyzer. Insufficient water flow inside the electrolyzer affects the cooling process. Consequently, the electrolyzer membrane dries out, leading to an increase in cell temperature. This, in turn, creates hotspots within the electrolyzer, ultimately resulting in failure.
- **Formation of flammable mixture:** Electrolyzer failure due to degradation can result in formation of hydrogen-oxygen gas mixture. In addition, specific operating conditions such as lower current density, higher operating temperature and higher current density can increase hydrogen concentration in the oxygen side. Cross over of both oxygen and hydrogen gases occurs at elevated pressure.

5. Conclusion

Green hydrogen produced by water electrolysis process is a promising solution for achieving carbon neutrality. A HAZOP analysis is conducted in this study for a water electrolysis plant involving a PEM electrolyzer for improving safety and reliability of the plant. Through HAZOP, operability issues that impact the safe and smooth functioning of the plant are identified. The HAZOP table documents deviations for each sub-systems as well as the causes and consequences associated with each deviation. These deviations lead to three main consequences: reduced plant efficiency, PEM electrolyzer degradation, and the formation of flammable mixtures. Additionally, the study highlights the interconnectedness between the deviations and emphasizes the importance of investigating the auxiliary components. Overall, the HAZOP analysis offers valuable insights to prevent adverse consequences and enhance plant efficiency and reliability.

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