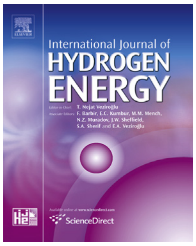
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Influence of process conditions on gas purity in alkaline water electrolysis

Philipp Haug[*], *Matthias Koj*, *Thomas Turek*

Institute of Chemical and Electrochemical Process Engineering, Clausthal University of Technology, Leibnizstr. 17, 38678 Clausthal-Zellerfeld, Germany

ARTICLE INFO

Article history:
Received 23 November 2016
Received in revised form
21 December 2016
Accepted 23 December 2016
Available online xxx

Keywords:
Alkaline water electrolysis
Gas purity
Process management
Hydrogen production
Gas solubility

ABSTRACT

In this paper the influence of operating conditions on the product gas purity of a zero-gap alkaline water electrolyzer was examined. Precise knowledge of the resulting gas purity is of special importance to prevent safety shutdown when the electrolyzer is dynamically operated using a renewable energy source. The investigation in this study involves variation of temperature, electrolyte concentration and flow rate as well as different electrolyte management concepts. The experiments were carried out in a fully automated lab-scale electrolyzer with a 150 cm^2 zero-gap cell and approximately 31 wt% KOH at ambient and balanced cathodic and anodic pressure. The purity of the evolved gases was measured via online gas chromatography. It can be seen from the experiments that a temperature increase and flow rate decrease reduces the gas impurity when mixing catholyte and anolyte. A further reduction of gas impurity can be achieved when both cycles are being separated and a dynamic cycling strategy is applied.

Introduction

In 2002 the German government set the goal to reduce CO_2 emissions by 80% until 2050 and to increase the contribution of renewable energy sources to the total electricity demand above 60% [1,2]. For the realization of this objective it is inevitable to establish energy storage devices to compensate the fluctuating nature of wind and solar energy [3–5]. Especially for long-term energy storage energy-rich hydrogen is commonly considered the most promising intermediate or final energy carrier [6–8]. Nowadays hydrogen, which is required in huge quantities for many important industrial processes such as ammonia synthesis, is still being produced through inexpensive, but greenhouse gas emitting processes like steam reforming and coal gasification [9–11]. Hydrogen production through electrolysis represents a share of only 4% which already reveals that water electrolysis is still too costly because of its limited energy efficiency and large investments [12]. But within the framework of the power-to-gas concept, particularly water electrolysis is often discussed as the key technology for future synthesis of hydrogen because of its fast dynamic response to varying operating conditions [13]. Especially alkaline water electrolysis has been applied in the industry for decades but the dynamic behavior was of minor interest until first investigations came up in the 1990s [14,15]. For realization and improvement of the power-to-gas-concept precise knowledge especially about the dynamic behavior of the electrolysis process is indispensable. During alkaline water electrolysis H_2O is reduced to H_2 and OH^- ions on the

---

[*] *Corresponding author*. Fax: +49 (0) 5323 72 2182.
E-mail address: haug@icvt.tu-clausthal.de (P. Haug).

http://dx.doi.org/10.1016/j.ijhydene.2016.12.111

cathode, whereas OH^- is oxidized to form O_2 and H_2O on the anode. In total H_2O is split into H_2 and O_2. The following Equations (1)–(3) show the half cell and overall reactions with their corresponding electrode potentials against a standard hydrogen electrode (SHE) at 298.15 K and pH = 13.996 [16].

$$\text{Cathode}: \quad 2\,H_2O + 2e^- \rightarrow H_2 + 2\,OH^- \quad E^0 = -0.8280\ \text{V} \tag{1}$$

$$\text{Anode}: \quad 2\,OH^- \rightarrow 0.5\,O_2 + H_2O + 2e^- \quad E^0 = +0.4011\ \text{V} \tag{2}$$

$$\text{Overall reaction}: \quad H_2O \rightarrow H_2 + 0.5\,O_2 \quad E^0 = -1.2291\ \text{V} \tag{3}$$

As can be seen from the overall reaction a minimum cell voltage of −1.2291 V, also referred to as reversible potential, is necessary for hydrogen production. In addition to this potential the overpotentials of the electrodes, the separator resistance and the bubble resistance have to be overcome as well [9]. Many workers are focusing on the improvement of the catalytic activity of electrode materials to reduce these overvoltages. A review of promising electrode materials and further optimization strategies for zero-gap electrolyzers was published by Pletcher and Xiaohong [17]. Not only the cell voltage of an electrolyzer but also the purity of the gaseous products is of major interest as these limit the operation range of the plant. In literature the acceptable part-load operation of an industrial alkaline water electrolyzer is typically given with 10–40% of the nominal load [18–22]. Below this working range the oxygen quality is significantly reduced through contamination of hydrogen and vice versa. One source of this contamination is the diffusion of the product gases through the separator. This does not only decrease the gas quality, but also the overall electrical efficiency of the electrolyzer as oxygen can react back to water with hydrogen present at the cathode. The second source of contamination is the dissolution of gas in the electrolyte. After saturation with the corresponding gas, dissolved gas is able to outgas in the opposite gas separator as the anolyte and catholyte cycle are continuously mixed to compensate the difference in electrolyte concentration caused by the electrode reactions (cf. Equations (1)–(3)) [23,24]. This operation mode may lead to safety issues as the lower (LEL) and upper explosion limits (UEL) of H_2/O_2 mixtures are given with 3.8 mol% and 95.4 mol% H_2 at atmospheric pressure and 80 °C [25]. Consequently industrial electrolyzers must be shut down as soon as a content of 2 vol% foreign gas is measured in the exhaust, which is about 50% of LEL or UEL [26]. The contamination of the product gases is of special importance when the electrolyzer is operated at low current densities and therefore low gas production rates because the mentioned phenomena are mostly independent of the electrolyzer load [23]. An operation in the part-load region is conceivable when the electrolyzer is part of a power-to-gas plant and coupled with a renewable energy source. Hug et al. [14] reported that the daily operation of an alkaline electrolyzer powered with solar energy was mainly restricted by the oxygen purity at low global insolation and the resulting low current density. A possibility to reduce the anodic hydrogen content was mentioned by Grigoriev et al. [27] who proposed a Pt-catalyzed combustion of hydrogen and oxygen back to water by a gas recombiner. Another option was published by Schug [23] who proposed an optimized lye circulation control to keep the gas impurities low. Unfortunately only the qualitative description of this effect was described whereas the quantitative influence of the electrolyte flow rate on the gas purity was not published. Further work was done by Manabe et al. [28,29] who measured the anodic hydrogen content at specific electrolyte temperatures and flow rates with different separators.

In the present work the mechanisms and the extent of gas crossover are discussed first. Then the operating conditions of a lab-scale electrolyzer, such as current density, electrolyte flow rate, temperature, electrolyte concentration and process management are varied systematically and analyzed with regard to the resulting gas purity to derive optimum operating conditions. For this purpose a detailed study is performed so that the influence of each single parameter on the gas purity can be indicated. Furthermore the dynamic response of the gas purity during changing operating conditions is investigated.

Gas crossover

The gas crossover in alkaline water electrolysis is mainly caused by two phenomena – gas dissolution in the electrolyte and diffusion through the separator. In the following it is shown how either of these sources may be estimated quantitatively.

Gas solubility

In reaction engineering the solubility of gases in electrolyte solutions needs to be known for gas–liquid transfer estimations [30]. Unfortunately data for the solubility of hydrogen and oxygen in concentrated potassium hydroxide solution under electrolysis conditions is scarce. Most published papers only provide values for the solubility at room temperature or slightly above. Ruetschi and Amlie [31] measured the H_2 solubility in KOH at 30 °C for a concentration range from 0.0091 to 10.23 mol L^{-1}, while Davis et al. [32] investigated the O_2 solubility and diffusivity in KOH for temperatures between 0 and 60 °C and concentrations of 0–12 mol L^{-1}. Further data of oxygen solubility in several inorganic solutions was published by Tromans [33] and Narita et al. [34]. Only two publications were found which deal with the hydrogen or oxygen solubility under electrolysis conditions. Chatenet et al. [35] measured the oxygen solubility in sodium hydroxide and found that the Henry coefficient of O_2 in 11.1 mol L^{-1} NaOH (33 wt %) at 80 °C was reduced by a factor of 72 compared to an electrolyte of 1 mol L^{-1} NaOH at 25 °C. The other publication by Knaster and Apel'baum [36] provides values for the oxygen and hydrogen solubility in concentrated KOH at 21, 45 and 75 °C.

To estimate the amounts of dissolved gases under electrolysis conditions we propose a method for calculation. It is well known that gas solubility mostly decreases with increasing salt concentration. This behavior can be described by applying the Setchenov relation (4), which is suitable for electrolyte concentrations of about $c_s = 2–5$ mol L^{-1}. At even higher salt concentrations the gas solubility may be underestimated [30].

Please cite this article in press as: Haug P, et al., Influence of process conditions on gas purity in alkaline water electrolysis, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2016.12.111