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INVESTIGATION ON WALL TEMPERATURE FLUCTUATIONS DURING HYDROGEN PRODUCTION BY ELECTROLYSIS

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Abstract. *This experimental study examined the wall temperature of the cathode during water electrolysis in an alkaline solution (30% wt KOH between 17 °C and 18 °C) under varying current densities. The research employed vertical electrodes with different gaps in a glass electrolyzer. A thermocouple E-type was attached to the cathode's outer wall to monitor temperature changes during nucleate onset and bubble release. The investigation focused on electric current densities ranging from 36.5 to 225 A/m². A CCD camera was used to analyze buoyancy-driven bubble dynamics along the cathode wall. The study observed increased velocity and vorticity fields, leading to heightened turbulence. The application of electric current led to an electrical resistance in the electrodes, causing the wall temperature to rise by up to 21.5 °C with fluctuations of approximately 0.5 °C. The presence of hydrogen bubbles on the wall further contributed to temperature increases, with fluctuations occurring due to bubble release over time. An optical flow method was implemented to investigate vorticity fields derived from the image sequence, as bubble-driven convection and convective mass transfer intensified with higher current densities. Turbulence-induced complex structures significantly impacted bubble dynamics. These findings enhance our understanding of the transport phenomena of hydrogen bubbles in the electrolyzer.*

Keywords: *Hydrogen Generation, Renewable Energy, Electrolysis, Temperature Fluctuations*

1. INTRODUCTION

In recent years, there has been growing concern over various aspects related to energy generation and transformation, particularly due to their environmental implications. As a result, the urgency to develop more sustainable sources of energy has garnered significant attention. For this reason, green hydrogen generated through electrolysis has become an attractive candidate due to its low environmental impact and high calorific value. However, several challenges related to increasing efficiency in hydrogen generation through electrolysis still need to be overcome.

Numerous researchers have devoted their studies to modeling hydrogen generation, incorporating both theoretical and experimental observations. Some notable contributions in this field include the works of Ehrl et al. (2013), El-Askary et al. (2015), Schillings et al. (2015), and Hreiz et al. (2015). Additionally, the impact of pressure has been explored by Vogt (2017), while temperature effects have been investigated by Olivier et al. (2017) and Lohmann-Richters et al. (2021). Furthermore, the volume of hydrogen generated has been examined by Haug et al. (2017).

In the process of water electrolysis, electrons move from the anode to the cathode, where they combine with hydrogen ions to produce hydrogen gas. As a result, the dissolved gas gradually accumulates until it reaches a critical state of supersaturated concentration on the electrode surface, leading to the formation of bubbles. This phenomenon of bubble nucleation has been documented by Jones et al. (1999) and Van Damme et al. (2010).

From the nucleation site, the gas bubble develops, potentially covering other possible sites. This hinders ion contact with the surface, suppressing the formation of new hydrogen bubbles. Only after the departure of the bubble does the re-wetting of the surface by the electrolyte occur again (Vogt, 2017).

Convection can occur naturally due to buoyancy or as a result of forced convection, while diffusion arises from concentration gradients of reactants and products between the electrode-electrolyte interface and the bulk. Consequently, extensive research efforts have been dedicated to investigating the dynamic behavior of the gas phase, including the impact of convection, velocity profiles, bubble formation, and the influence of various parameters such as current density, electrode gap, concentration, temperature, pressure, among others. Numerous experimental studies have been reported in the literature, exploring different aspects related to water electrolysis, particularly focusing on the fundamental fluid dynamics of bubbles. To achieve this, various experimental techniques have been employed to visualize velocity fields and bubble growth, including Particle Image Velocimetry (PIV), Laser Doppler Velocimetry (LDV), Laser-Induced Fluorescence (PLIF), Particle Tracking Velocimetry (PTV), and others. Abdelouahed et al. (2014) conducted a study on the hydrodynamics of gas bubbles during water electrolysis using NaOH as the electrolyte. The researchers examined the distributions of bubble velocities and void fractions in the anode-to-cathode space. They investigated the influence of the anode gap, current density, and cell inclination on the hydrodynamics of the gas phase. Zhu et al. (2018) conducted a comprehensive investigation into the hydrodynamic behavior and mass transfer performance in water electrolysis processes using two distinct container and electrode configurations across various current densities. The authors employed PIV method to capture the velocity field, and their findings indicated that the mean vertical velocity escalates with rising current density. Moreover, they observed that higher current densities enhance natural convection due to the generation of Joule effect. Babu and Das (2019) conducted a detailed investigation on the mass transfer processes taking place at the electrode-electrolyte interface of a water-splitting electrochemical cell. They utilized PIV and PLIF techniques to examine the instantaneous velocity and concentration fields. The authors specifically focused on the influence of cell voltage, electrode orientation, and the concentration gradient resulting from reactant depletion and product formation at the interface on the mass transfer rate. The experimental study encompassed various current densities and electrode orientations. The observations unveiled that even at low current densities, reactant depletion and product formation at the anode interface induced buoyancy effects, leading to natural convection. Despite the numerous efforts documented in the literature regarding the production and transportation of hydrogen in electrolysis, comprehending the dynamics of bubbles during this process remains a challenge. One of the main difficulties lies in understanding the dynamics of the two-phase flow within the electrolyte, driven by the convective and vorticity zones induced by the turbulent nature of the phenomenon. Therefore, this study aims to investigate both velocity fields and cathode wall temperature during alkaline water electrolysis with a specific focus on considering the impacts of current density and electrode gap.

2. EXPERIMENTAL FACILITY AND METHODOLOGY

In Figure 1, the experimental setup for investigating bubble dynamics is described. The setup includes a test section that comprises a cubic container with an edge length of 80 mm. A DC power supply model Minipa MPL-3305 is used in the setup. The working electrodes in the setup are made of stainless steel 304, which contains 19% chromium and 9% nickel. The selection of this material is based on its stability in an alkaline medium, indicating that it can withstand and maintain its properties in an alkaline environment. Both electrodes in the setup have dimensions of 30 mm in width and 70 mm in length. They are arranged vertically with a gap of 20 mm between them. This arrangement allows for the study of bubble dynamics in the test section. The experiment took place at approximately room temperature, which is around 20°C. A 30%wt KOH aqueous solution in deionized water was used. The specific experimental parameters can be found in Table 1. To capture images, a CCD camera model DSRL EOS with a resolution of 2048 x 2048 pixels and a 50 mm lens was employed. With this image resolution, the smallest length scale corresponded to 74.4 μm/pixel. The camera had a capture rate of 120 frames per second. To measure the temperature of the electrode wall, a type E thermocouple is attached to the external wall of the electrode using a nylon cable tie, as shown in Figure 1 (b).

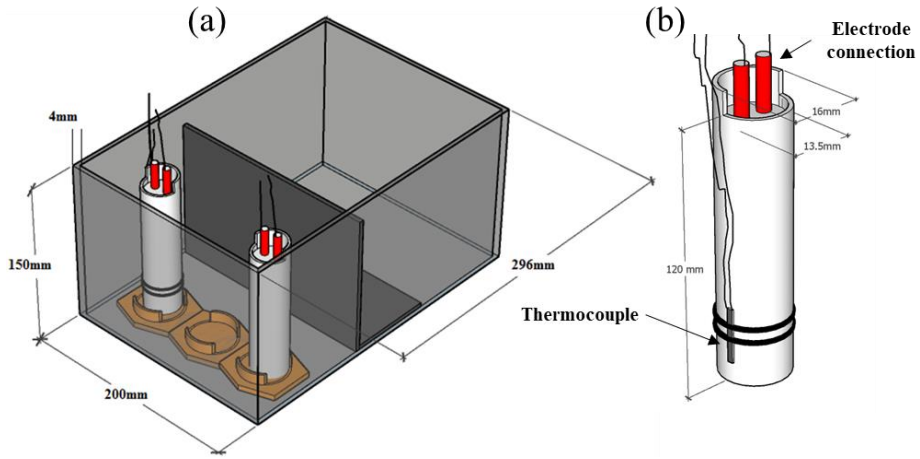

Figure 1. (a) Electrolyzer; (b) Position of thermocouple stuck on the external surface of cathode.

Table 1. Experimental conditions.

Properties and Parameters	Value/Range
Molar mass [mol/l]	5.4
Density of electrolyte [kg/m³]	1237
Viscosity of electrode [kg/(m·s)]	$1{,}731 \times 10^{-3}$
Current density [A/m²]	36.5 – 225.3
Electrolyte temperature [°C]	17 and 18
Gap between electrodes [mm]	30 and 70

2.1 Chemistry of water electrolysis

The electrolyte used in the experiment is a diluted solution of potassium hydroxide (KOH), which dissociates into K+ and OH- ions. As a result, oxygen gas is produced at the anode, while hydrogen gas is generated at the cathode. This electrochemical reaction occurs at the anode (oxidation):

$$4OH^- \rightarrow \mathrm{O_2(gas)} + 4\mathrm{e}^- + 2\mathrm{H_2}O, \tag{1}$$

and at the cathode (reduction):

$$4H_2O + 4\mathrm{e}^- \rightarrow 2\mathrm{H_2}(gas) + 4OH^- \tag{2}$$

2.2 Optical Method

The optical flow technique relies on Liu and Shen's (2008) approach, which takes into account the optical flow equation and its application to various flow visualizations, expressed in terms of image coordinates:

$$\frac{\partial g}{\partial t} + \nabla \cdot (g\boldsymbol{u}) - f(x, y, g) = 0 \tag{3}$$

In this equation, g represents the normalized image intensity, which is directly proportional to the radiance detected by the camera. The velocity in the image plane, denoted as $\boldsymbol{u} = (u_x, u_y)$, is referred to as the optical flow. The function $f(x, y, g)$ represents a term associated with boundaries and diffusion. The operator $\nabla \equiv {}^{\partial}/_{\partial x_i}$ represents the spatial gradient The optical flow u is proportional to the light-path-averaged velocity, weighted by the field quantity Φ, which is related to the visualizing medium. Generally, the optical flow is not divergence-free, *i.e.*, $\nabla \cdot \boldsymbol{u} = 0$. But when the term $g\nabla \cdot \boldsymbol{u} = 0$, Eq. (3) is reduced to the Horn-Schunck brightness constrain equation, given by

$$\frac{\partial g}{\partial t} + g\nabla \cdot (\boldsymbol{u}) = 0 \tag{4}$$

To determine the optical flow, a variational formulation is employed, incorporating a smoothness constraint. This formulation is expressed through a functional described in Eq. 5.

$$j(\boldsymbol{u}) = \int_{\Omega} \left\{ \left[\frac{\partial g}{\partial t} + \nabla \cdot (g\boldsymbol{u}) \right]^2 + \lambda \left(|\nabla u_x|^2 + |\nabla u_y|^2 \right) \right\} dxdy \quad (5)$$

where λ represents the Lagrange multiplier, and **Ω** denotes the image domain. By minimizing Eq. 6, Euler-Lagrange equation is obtained:

$$g\nabla \left\{ \frac{\partial g}{\partial t} + \nabla \cdot (g\boldsymbol{u}) - f \right\} + \lambda \nabla^2 \boldsymbol{u} = 0 \quad (6)$$

The solution to Eq. 6 is obtained using the standard difference method, subject to the Neumann condition $\partial \boldsymbol{u}/\partial n = 0$ on the image domain.

3. RESULTS

3.1 Velocity fields

For all tests, it was considered a sequence of 10 images to obtain the average velocity field. Figure 3 presents the fifth image from the sequence and the respective average velocity field for *J* of 36.5 and 225.3 A/m². As it can be seen, the velocity field is influenced by both the electrode gap and the applied current density. The highest intensities of the average vertical velocity can be observed for the 30 mm gap, regardless of the applied current density. Velocity field analyses based on different image sequences also indicate fluctuations along the cathode surface. These fluctuations result in the formation of vorticity, increasing the wetting effect of the surface and enhancing the bubble detachment rate of hydrogen near the surface.

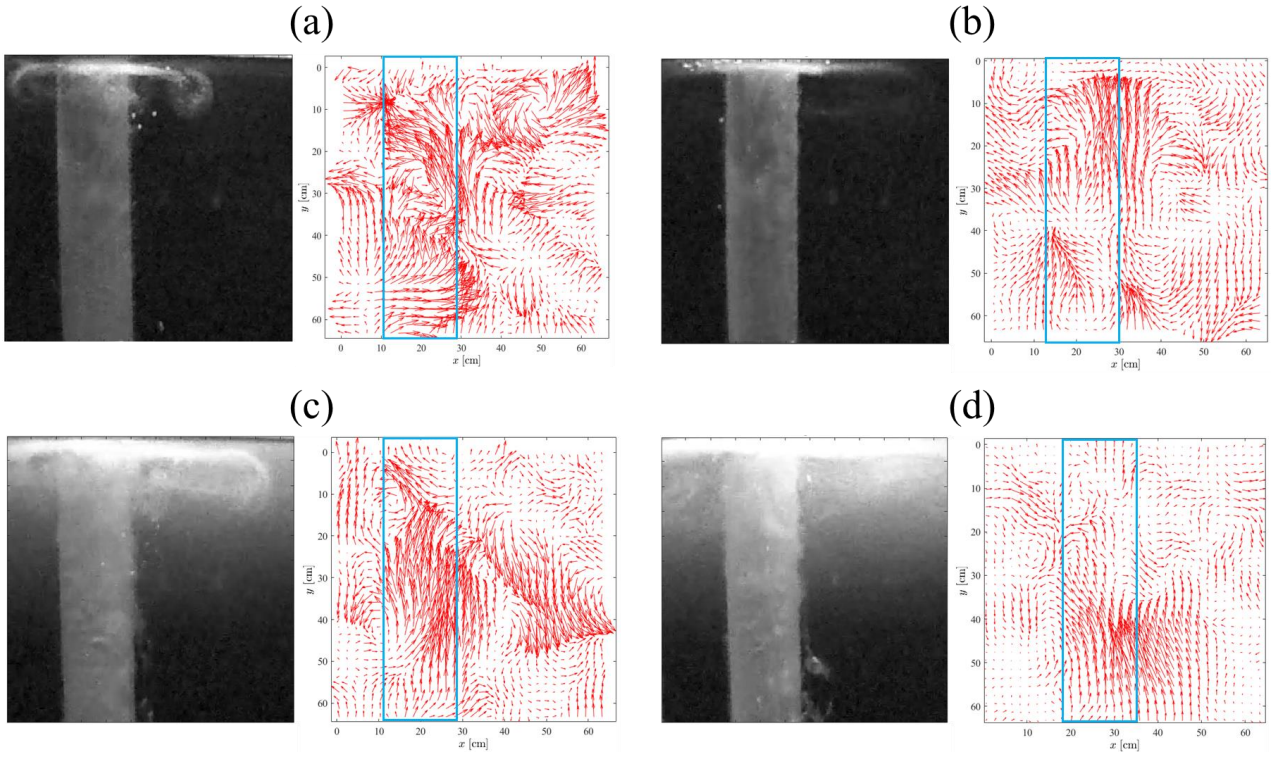

Figure 2. Velocity field for: (a) *J* = 36. 5 A/m² and gap of 30 mm; (b) *J* = 36. 5 A/m² and gap of 70 mm; (c) *J* = 225.3 A/m² and gap of 30 mm; (d) *J* = 225.3 A/m² and gap of 70 mm. The region of electrode is outlined in blue;

3.2 Fluctuations of wall temperature

Since the cathode-electrolyte-anode assembly corresponds to electrical resistances to the passage of charge carriers during electrolysis, an increase in temperature is mainly observed at the electrode-electrolyte interface. The bubble release and, consequently, wetting cause temperature fluctuations on the external surface of the cathode. To measure the wall temperature, a E-type thermocouple attached to the external wall of the cathode at a height of 20 mm from the base was

installed. Another E-type thermocouple, immersed in the electrolyte, was also used to measure bulk temperature. Figure 3 shows the wall temperature fluctuations at the cathode over time.

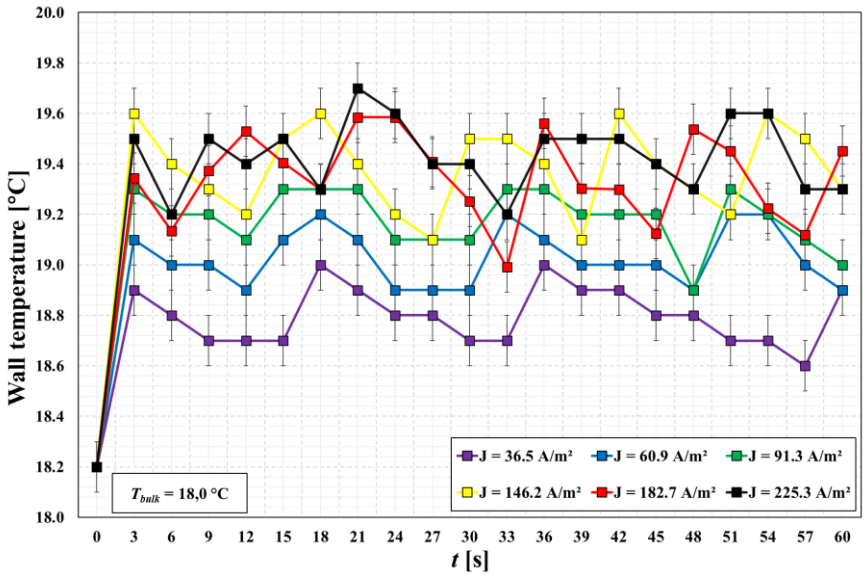

Figure 3. Temperature fluctuations over time under different current densities.

These fluctuations, caused by both velocity field fluctuations and surface re-wetting after bubble detachment, exhibit a dependency only at low current density (36.5 A/m²). However, increasing the current density raises the surface temperature until the onset of bubble departure (t < 3 s). Figure 4 presents the average surface temperature of the cathode as a function of current density for a test with a bulk temperature of 17°C for both gaps.

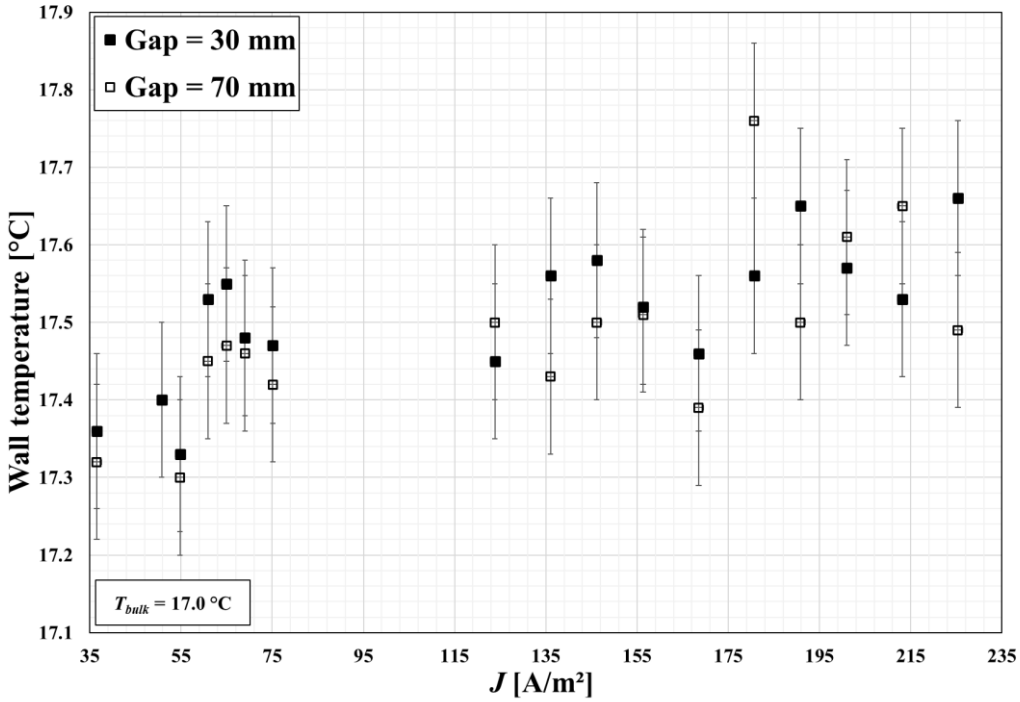

Figure 3. Average wall temperature for different current densities.

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5. RESPONSIBILITY NOTICE

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