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# Bubble Over-Potential During Two-Phase Alkaline Water Electrolysis

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ABSTRACT

During two-phase water electrolysis production of bubbles at one or both electrodes is observed. This leads to a change in the electrolyser electrical and hydrodynamic properties. When gravity is present, the production of bubbles at the electrodes induces a macro-convection in the electrolyser. This leads to a local distribution of the bubbles determining the local gas void fraction and current density at the electrodes. The absence of gravity eliminates the natural convection and buoyancy forces and consequently the frictional forces. It is generally difficult to estimate the quantitative influence of each of these single phenomena due to strong coupling. In the present work, alkaline water electrolysis is performed. The formation of gas bubbles at the anode is observed using four cameras. The aim of this study is to establish the quantitative evolution laws for the electrochemical cell potential, the bubble diameter and population density during alkaline (NaOH) two-phase electrolysis in function of the two explored inputs current density and gravity.



## 1. Introduction

In the literature few works concerning experimental and theoretical studies on two-phase electrolysis are reported although several important industrial processes are involved such as hydrogen, fluorine, chlorine, and aluminum production. The over-potential due to bubbles is generally described with an added Bruggeman resistance related to an estimated gas-void fraction. The challenge is to have an accurate estimation of the two-phase boundary layer thickness at electrodes to ensure a correct gas-void fraction $\varepsilon$ and resistance estimation. This boundary layer, under Earth condition in term of gravity G, yields to a vertical position dependent gas-void fraction. For this reason some research teams have demonstrated interest in theoretical and experimental studies under zero gravity condition, although such experiments are both difficult and expensive to perform. Matsushima et al. [1,2] observed oxygen and hydrogen gas evolution on platinum electrodes in alkaline and acid solutions during 8s under microgravity environment realized in a drop shaft. They reported that the effect of gravity level is more important in the case of KOH solution than in $H_2SO_4$ solution. They have also shown that in alkaline solutions, the current density j is much smaller under microgravity than under Earth gravity. Further they showed that the electrical resistance increases under zero-gravity due to the formation of a gas bubble layer and an increase in electrode surface screening by bubbles [1,2].

Brussieux et al. [3] have performed a study of gas release (hydrogen bubbles) during water electrolysis. The conclusion of this work is in good agrement with our previous work [4] and Vogt's theoretical results [5–7]. Vogt et al. [5–7] noted the influence of the flow velocity in a stagnant fluid and a forced or gravity induced fluid flow with speeds ranging from 0.01 to 0.3 m $s^{-1}$. It was further noticed that the gas fraction $\varepsilon$ decreases with increasing flow velocity. Numerical simulations carried out by Mandin et al. [8,9] under normal Earth gravity attempt to model the influence of bubble production onto the current density j distribution through a vertical position dependent gas-void fraction and electrical conductivity. This kind of work was completed and validated with the experimental work of Wüthich et al. [10,11] and Tobias et al. [12]. It has been shown that the two-scales free convections on Earth made difficult a correct primary or secondary two-phase electrolysis modeling. It was consequently decided to perform both experiments under zero and normal gravity condition in order to obtain accurate quantitative evidences for two-phase electrolysis modeling.

Concerning more specific zero gravity works, a decrease in overall cell performance is also observed for both methanol fuel cells and electrolysis reactor due to gas bubbles enlargement [13]. Kaneko or Guo et al. [14,15] also investigated water electrolysis under zero gravity condition and found that gas bubbles become larger and current densities decreased in microgravity. Their results suggest that during electrolysis the water species mass transfer

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**Nomenclature**

| | |
|---|---|
| δ | Electrode two-phase boundary layer thickness (m) |
| d | **Average bubble diameter (mm)** |
| Δd | Diameter standard deviation (mm) |
| E° | Thermodynamical standard RedOx potential (V) |
| ε | Gas bubble gas-void fraction (-) |
| G | Normal Earth gravity acceleration = **9.81** m $s^{-2}$ |
| j | Applied current density (A $m^{-2}$) |
| μ | Dynamic viscosity (Pa s) |
| N | **Bubble population** (bubbles $cm^{-2}$) |
| n | Bubbles number (-) |
| P | Pressure level |
| P° | Atmospheric pressure condition (1.013 $10^5$ Pa) |
| ρ | Density (kg $m^{-3}$) |
| S | Surface Area ($m^2$) |
| σ | Electrical conductivity (S $m^{-1}$) |
| T | Temperature in interval (about 295 K) |
| t | time (s) |
| θ | Electrode bubbles surface screening (-) |
| XG | Dimensionless gravity = -1 or +1 respectively for 1G or 0G level |
| Xj | Dimensionless current density = -1 or +1 respectively for min or Max j |

*Subscript*

| | |
|---|---|
| $O_2$ | Oxygen at anode. |
| P | Pixel. |
| ini | Initial. |
| end | Final, generally @ t = 20 s. |
| tot | total. |
| 0 | initial or bulk liquid electrolyte condition. |

to the electrode controls the process. However, under normal Earth gravity conditions, water electrolysis is said to be kinetically limited.

From the kinetics point of view, Iwasaki et al. demonstrate the faster establishment of a steady state for electrolysis current under normal gravity and free convection than under pure diffusion zero-gravity conditions [16].

More recently, in 2012, Nicolau et al. [17], using the Nasa Boeing for zero-gravity experiments, perform ammonia oxydation experiments.

The present study presents the evolution of the electrode bubble boundary layers produced during the two-phase electrolysis of an alkaline aqueous solution and its effect on the cell potential. Based on the analysis of the electrical signals and on the CCD post-processed videos (Figure 1), the goal is to relate the two-phase electrochemical cell terminal potential U with the two-phase boundary layer structure in term of bubble diameter d, standard deviation Δd, population N and on the gas-void fraction ε at the anode (Figure 1a).

Figure 2.

## 2. Experimental

Experiments for two different conditions of current density j and gravity G (9.81 m $s^{-2}$, normal Earth gravity and zero gravity) have been performed on vertical electrodes in a cubic electrochemical cell. A scheme of the present paper experimental strategy is presented in Figure 1b.

Experiments in microgravity were conducted in the NOVESPACE® Airbus A300 aircraft. The maximal acceleration was in the range from -0.05G to +0.05G. During the present

**Table 1**
Experimental design and 8 experiments definition.

| Exp. | Current Density Xj | Gravity XG |
|---|---|---|
| 1 | - | - |
| 2 | + | - |
| 3 | - | + |
| 4 | + | + |

When Xj = -1. j = 48 A $m^{-2}$
When Xj = +1. j = 80 A $m^{-2}$
When XG = -1. G = 9.81 m $s^{-2}$
When XG = +1. G = 0 m $s^{-2}$

**Table 2**
Liquid electrolyte properties at T = 298 K.

| NaOH Concentration mol $L^{-1}$ | NaOH Concentration g $L^{-1}$ | Density kg $m^{-3}$ | Conductivity S $m^{-1}$ |
|---|---|---|---|
| $1.0 \times 10^{-1}$ | 4 | $1.05 \times 10^3$ | 1.63 |

electrolysis gas production occurs at both electrodes according reactions (1) and (2):

Anode:

$$4OH^- \rightarrow O_2(g) + 2H_2O + 4e^- \quad E^0(HO^-/O_2) = 0.4V \qquad (1)$$

Cathode:

$$4H_2O + 4e\text{-} \rightarrow 2H_2(g) + 4OH^- \quad E^0(H_2O/H_2) = -0.83V \qquad (2)$$

The anode (nickel) and cathode (copper) material evolution reactions were neglected in the present work due to the short time the experiments lasted.

Experiments in microgravity and in the presence of gravity were conducted according to the experimental design presented in Table 1. Parameters studied were the current density j and the gravity level G (Erath- and zero-gravity). The current density j has been chosen between 48 and 80 A $m^{-2}$ which is about ten to one hundred times smaller than typically used current densities in industrial processes (between 0.1 and 1 A $cm^{-2}$). These smaller values have been chosen due to aircraft safety rules (minimize hydrogen evolution) and also to organize a modeling strategy from small to large current density values. Also a small alkaline NaOH concentration value has been chosen to obey safety rules inside the aircraft. The work was performed for each of these explored inputs for two levels values: -1 and +1, which are respectively the minimal and maximal values.

The used experimental set-up was presented in detail in [4,18]. The essential points are repeated here for convenience.

### 2.1. Electrochemical system

A battery of 30 identical electrolytic cells (25 mm x 25 mm x 25 mm) was employed. The electrodes surface area was 25 mm x 22.6 mm and the thickness was about 0.1 mm (Good Fellow®). The cathode was copper and the anode nickel. The supporting electrolyte was sodium hydroxide $10^{-1}$ mol $L^{-1}$ (Sigma Aldricht®). The liquid electrolyte properties are given in Table 2. The values have been experimentally obtained and are in good agreement with literature data. Density has been measured using a microbalance. Electrical conductivity has been measured using the C5010 Consort® apparatus. The measured value is in good accord with usual given values for such electrolyte.

The pressure inside the cells was controlled as described in detail in [4,18]. The pressure level inside the insulated double containment of the cells, though the aircraft pressure was about 0.8 Bars, was found quite constant at atmospheric condition P°=1.013 Bar.