Bubble Behavior on Horizontal and Vertical Carbon Anode Surfaces in Cryolite Melt Applying a See-Through Cell

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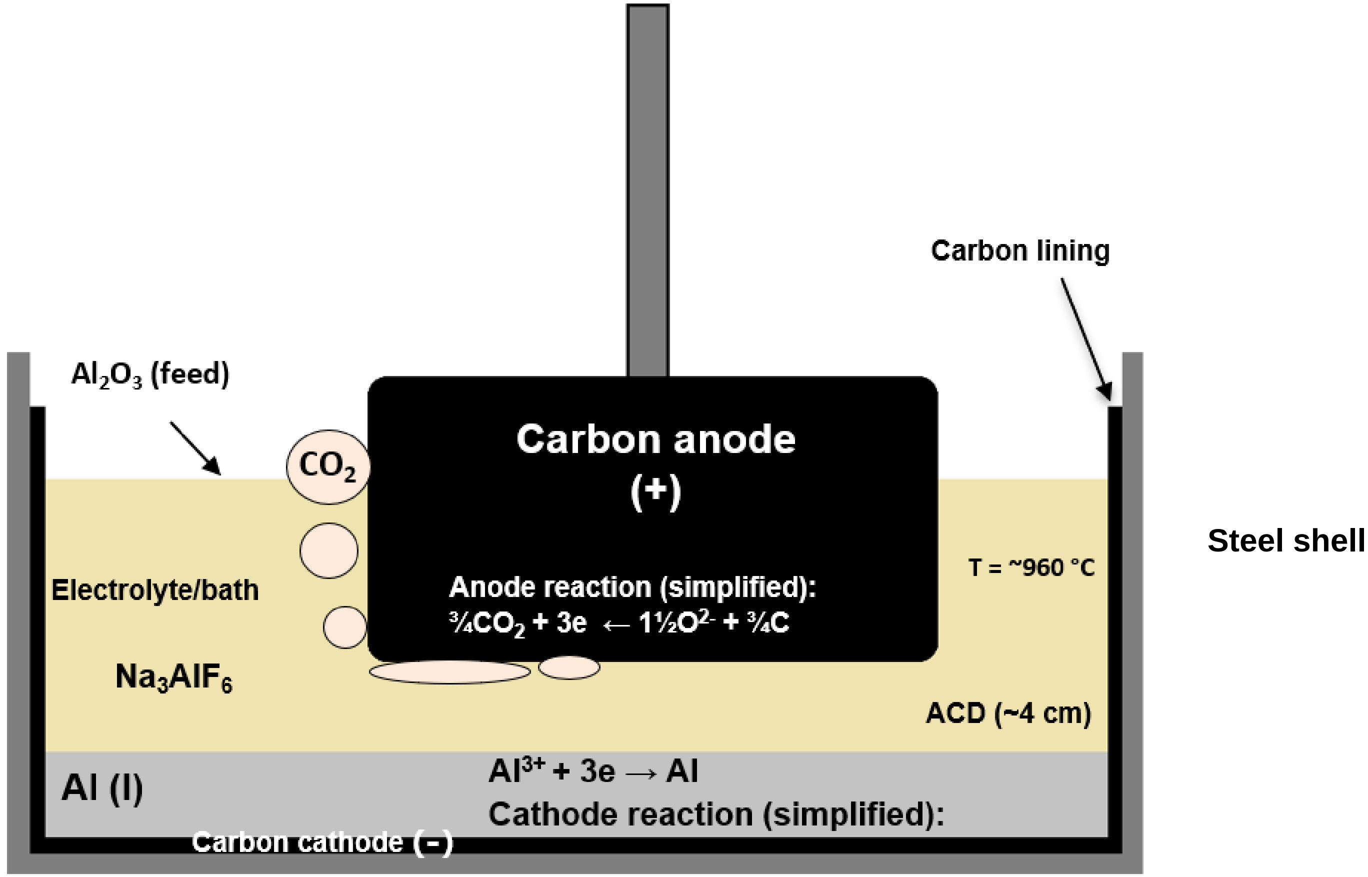
Introduction

Principles of the Hall–Héroult process

- Electrolytic reduction of aluminium oxide (alumina, Al_2O_3) dissolved in molten cryolite ($3NaF\text{-}AlF_3$)



Total simpflied reaction: $\frac{1}{2}Al_2O_3 + \frac{3}{4}C = Al + \frac{3}{4}CO_2$

- Gas present at the anode surface causes an additional voltage drop – bubble overvoltage

- The extra voltage drop due to bubbles is about 0.15-0.35 V out of a typical total cell voltage of ~4.5 V

- Reducing energy consumption in aluminium electrolysis is of major importance for production cost savings and for reduction of greenhouse gas emissions

- Anode bubble behavior for different anode designs and materials have been studied industrially and in lab.

- Laboratory scale experiments are typically used to study reaction kinetics and mass transport, anode effect phenomena, current efficiency, carbon quality properties, etc

- To interpretate results from the lab scale experiments it is important to understand how lab scale electrodes perform

- Due to the bubble evolution on the anode it is especially important to understand that process

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Aim of work

- Fundamental understanding of the bubble behavior on lab scale anodes

  - Study of bubble life cycle
    - Nucleation
    - Growth
    - Coalescence
    - Detachment

  - Influence of bubble evolution on current/potential

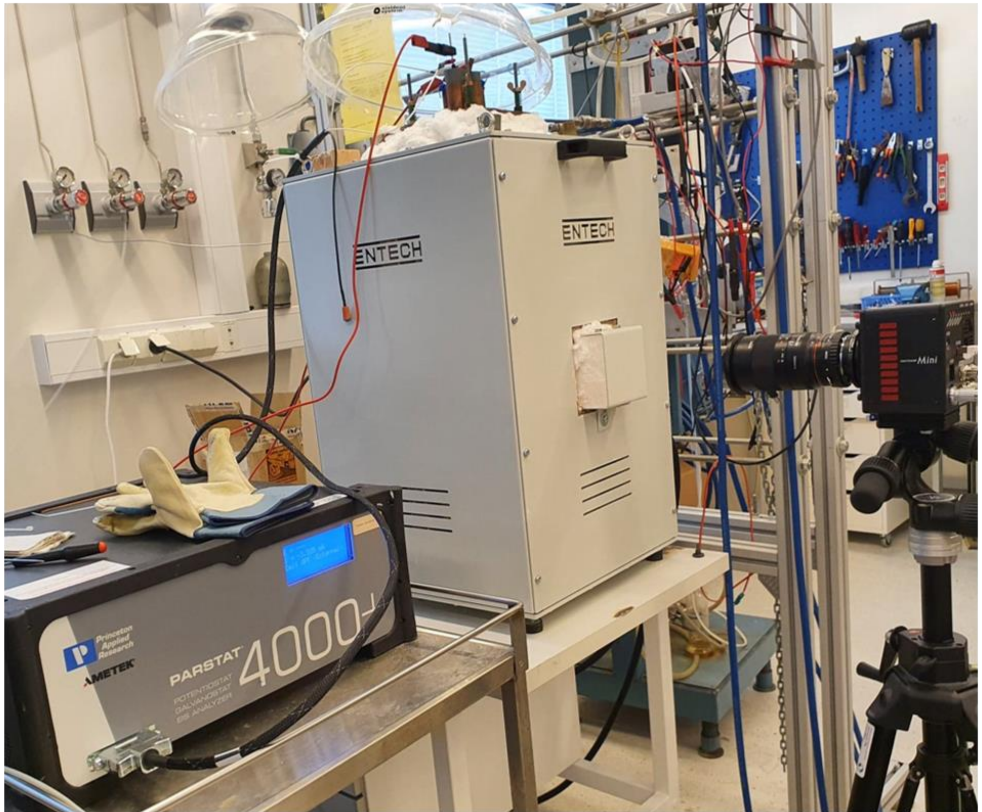
  - Quantification of
    - bubble size,
    - bubble layer thickness,
    - wetting angle, etc.

  - Application of different anode designs

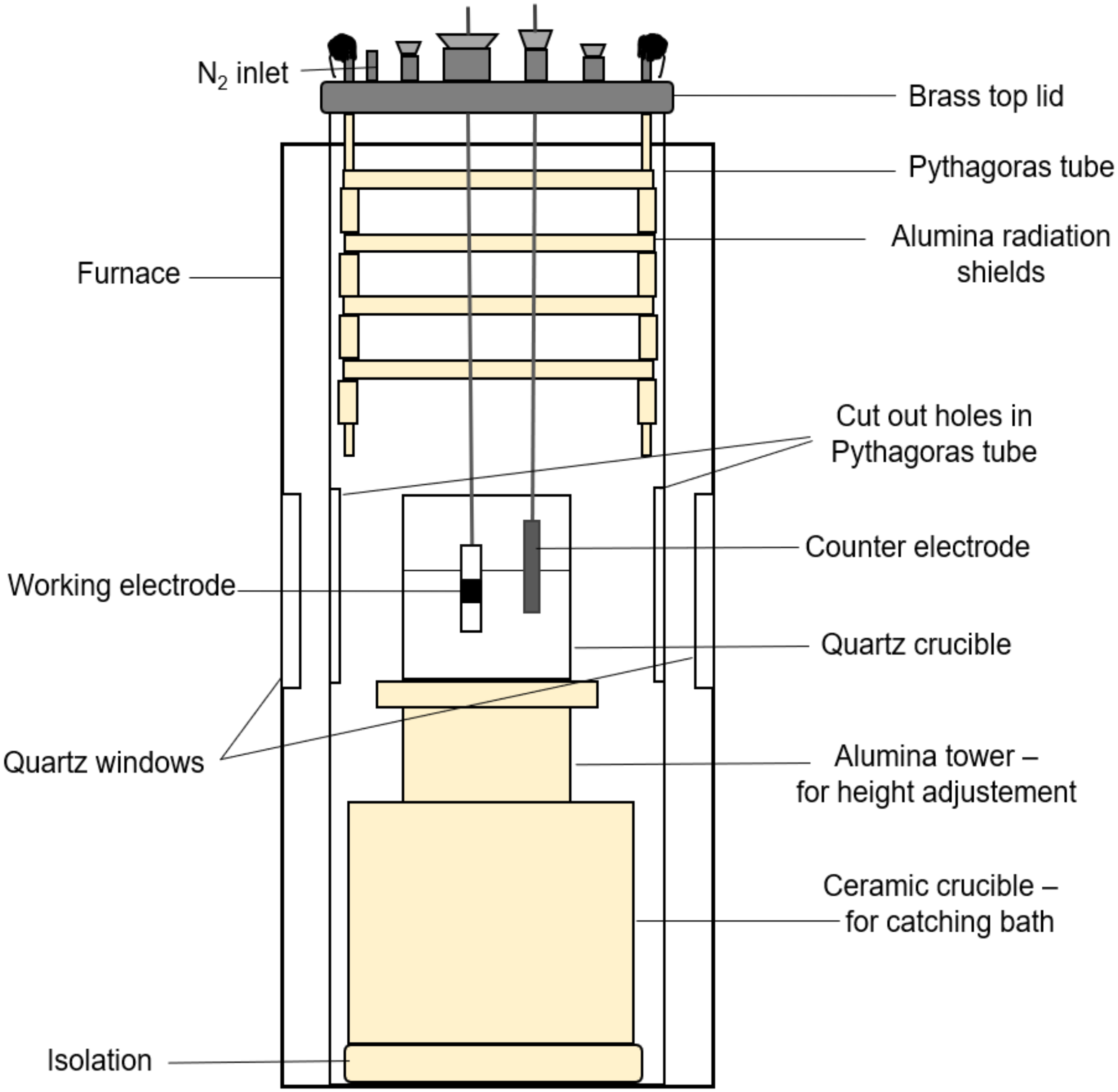
Experimental part

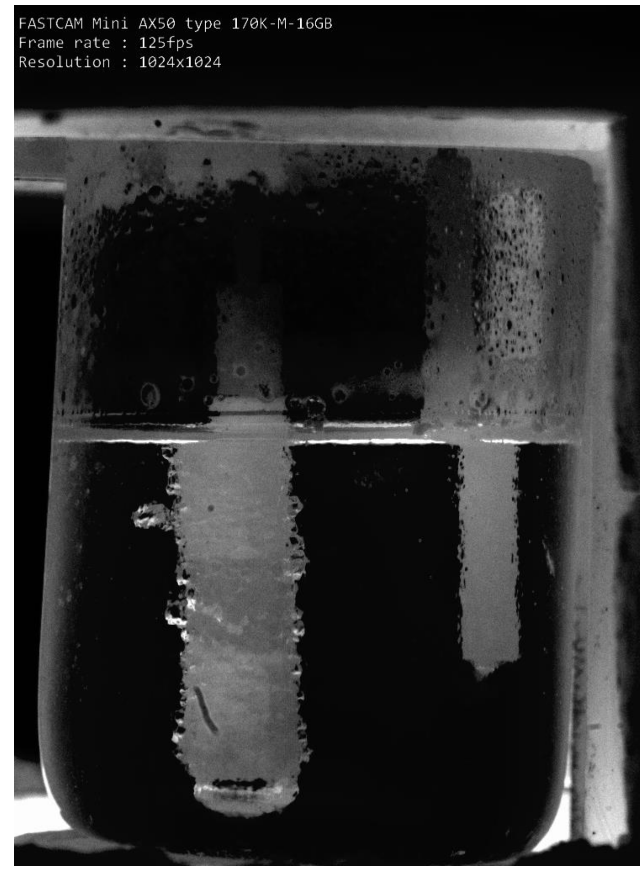
Experimental set up

- See-through furnace (customized furnace form ENTECH)
- High speed video camera (Photron Fastcam Mini AX camera)
- Potentiostat (PARSTAT) and booster (KEPCO)



Details of the cell



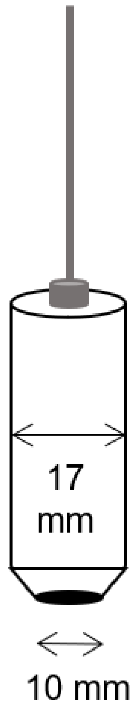


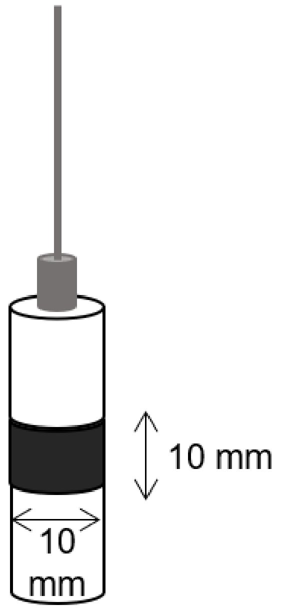
Bath composition and temperature

	wt %	Specification	Producer
Al_2O_3	3	γ-alumina	Merck
AlF_3	15	sublimed „“in house”	Industrial grade
LiF	15	purum	Riedel-de-Haën
CaF_2	5	precipitated pure	Merck
Cryolite	62	synthetic, purity > 97%	Sigma-Aldrich

- Calculated liquidus temperature: 838 °C
- Working temperature: 890±10 °C
- Superheat: ~ 50 °C

Anode design





Horizontal anode with the horizontal surface facing downwards

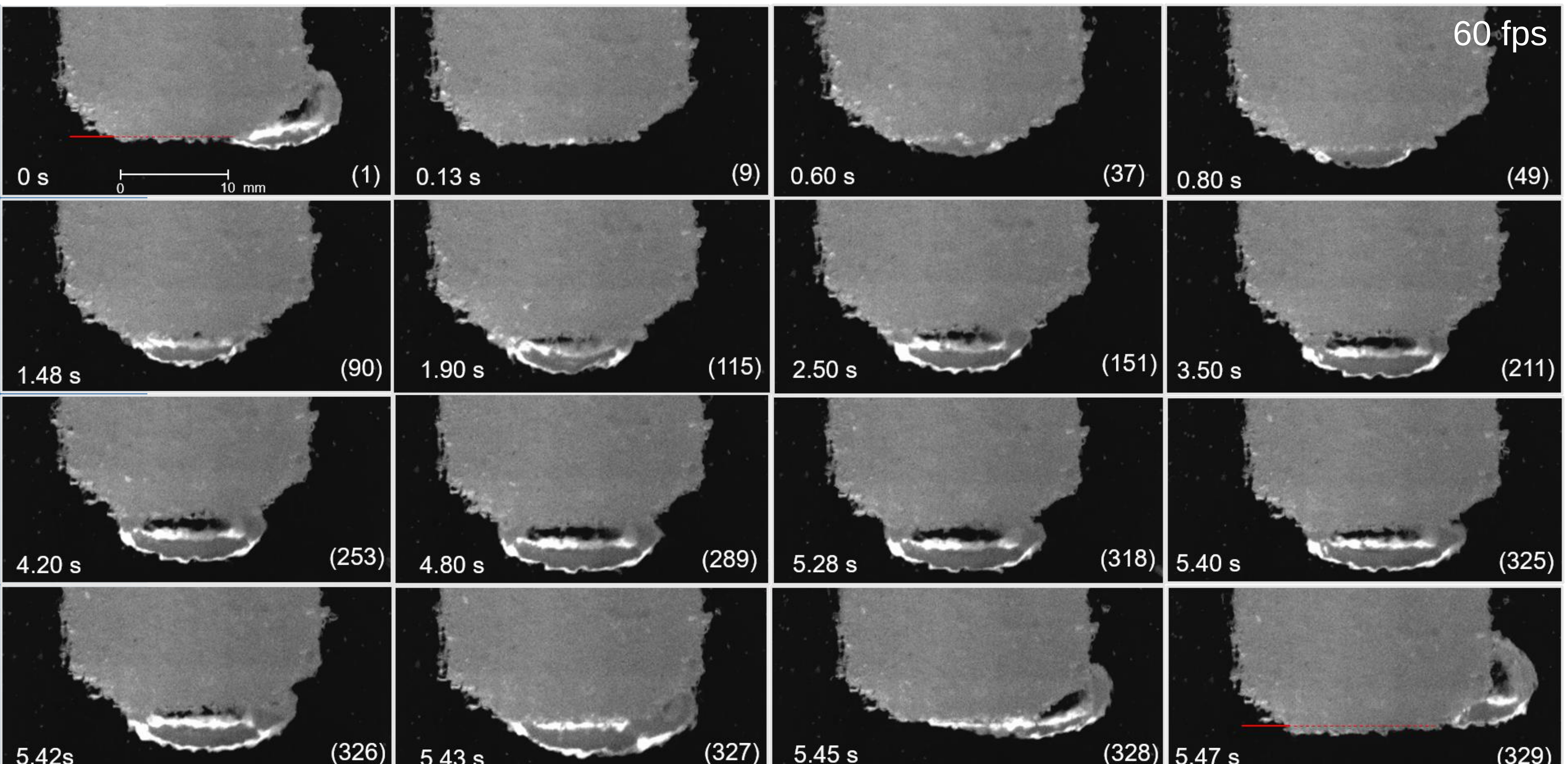
Vertical anode with the vertical surface

Results and disscusion

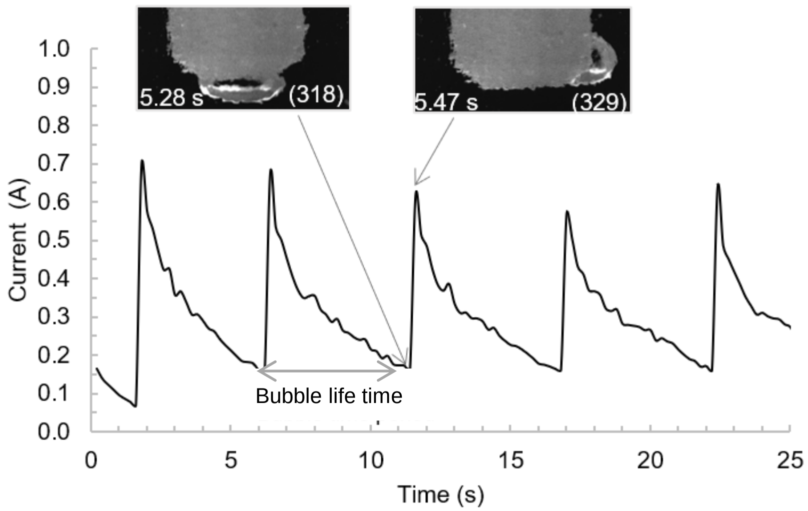
Bubble behavior on the horizontal anode

Bubble life cycle

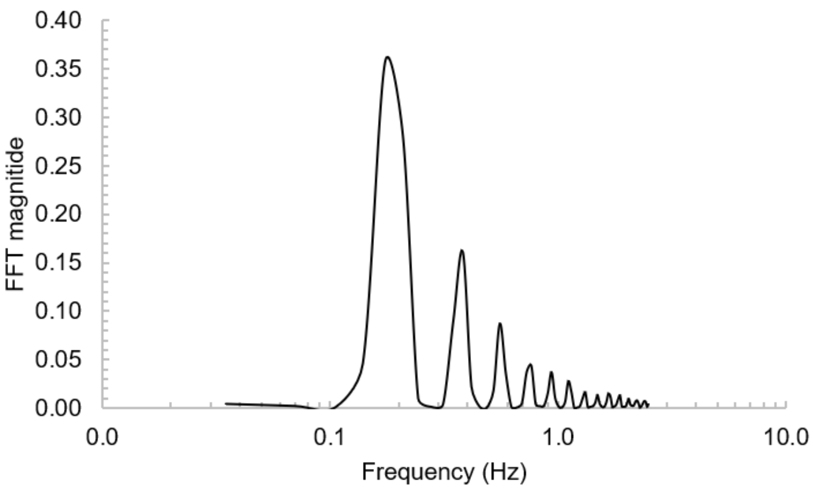
- Constant cell voltage 1.5 V, average current density 0.4 A cm^{-2}
- Bubble life cycle time 5.47 s



Bubble life cycle

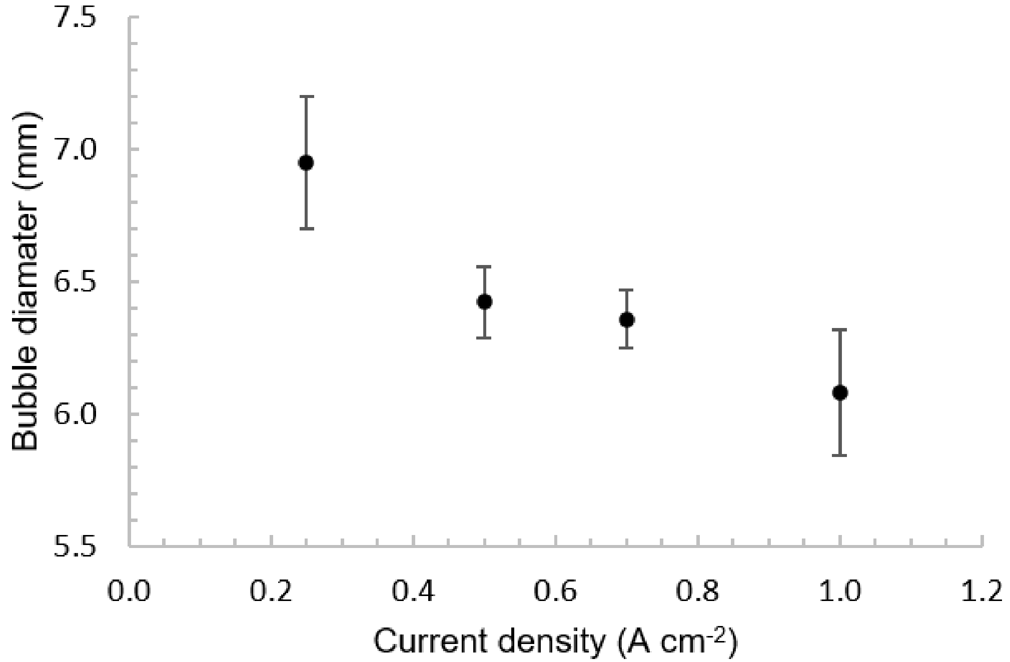


- Saw-tooth shaped curve of current vs. time data
- Bubble life time - ~5.5 s



- FFT spectra of current -time data
- Dominant frequency obtained with FFT analysis is 0.18 Hz which corresponds a 5.5 s bubble life time

Bubble size after detachment from the horizontal anode

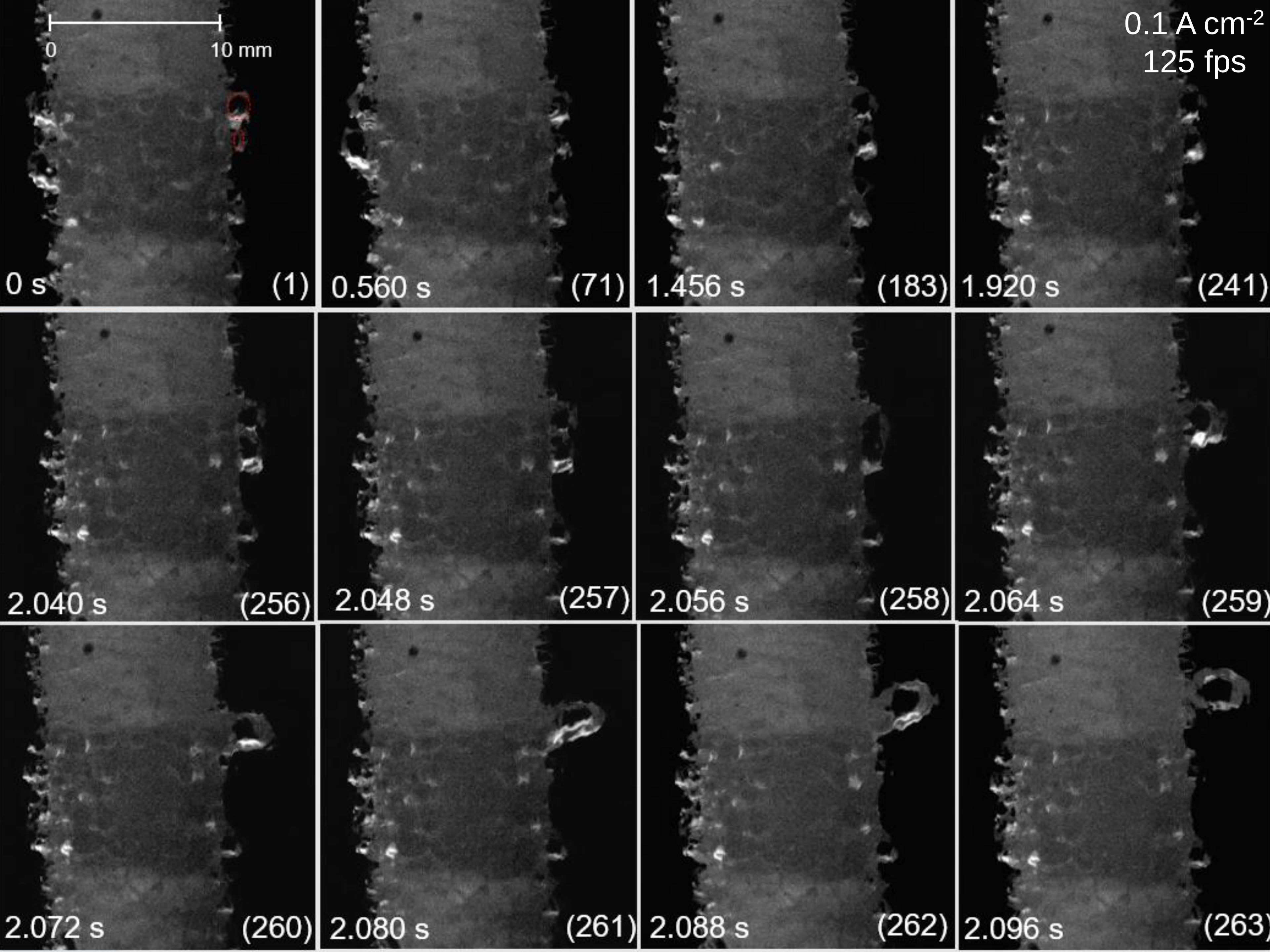


- Bubble diameter decreases with increasing current density
- The increase in current density and thereby the corresponding increase in potential give higher driving force for nucleation of relatively more bubbles
- Increased bubble induce convection

Bubble behavior on the vertical anode

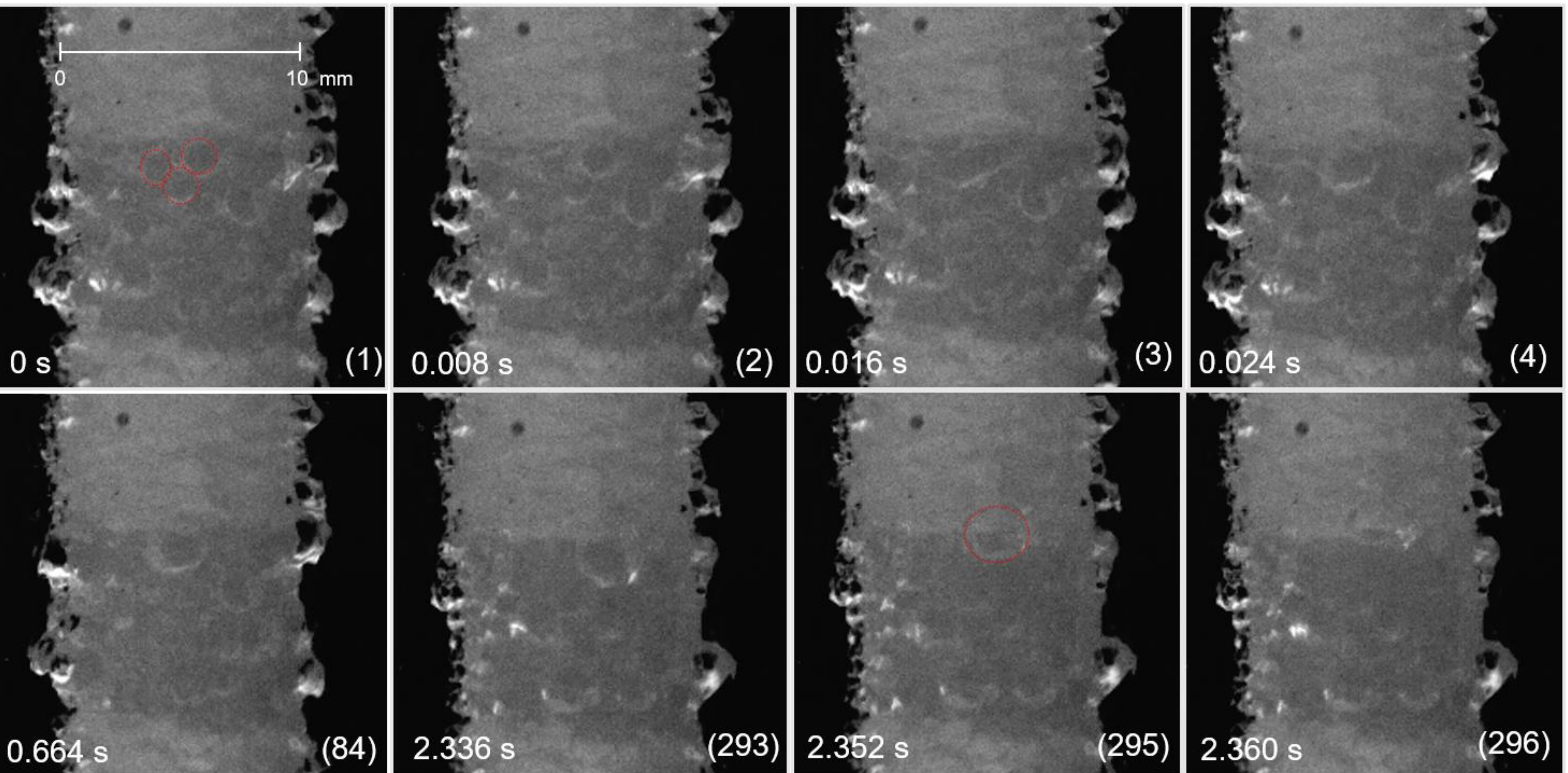
Coalescence and detachment of the bubble

- Example of coalescence of two bubbles into one larger bubble
- Immediate detachment of that bubble from the vertical surface

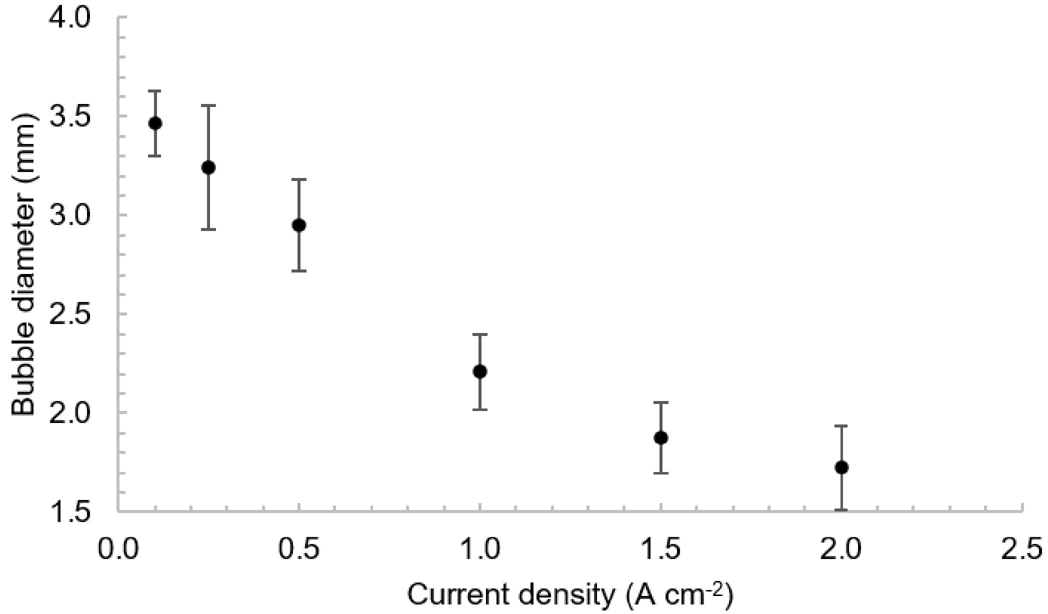

0
10 mm
0.1 A cm-2
125 fps
0 s
(1)
0.560 s
(71)
1.456 s
(183)
1.920 s
(241)
2.040 s
(256)
2.048 s
(257)
2.056 s
(258)
2.064 s
(259)
2.072 s
(260)
2.080 s
(261)
2.088 s
(262)
2.096 s
(263)

Coalescence and detachment of the bubble

- Example of coalescence of three bubbles into one larger bubble
- Long resting and growing of the bubble at the BN/C boundary



Bubble size after detachment from the vertical anode



- Bubble diameter decreases with increasing current density
- The increase in current density and thereby the corresponding increase in potential give higher driving force for nucleation of relatively more bubbles
- Increased bubble induce convection

Conclusions

- The bubble diameter decreased with the increasing current density for both the horizontal and the vertical anode.

- At the horizontal facing downwards surface the bubbles grew and coalesced to form one large bubble which then grew larger and finally started to slide toward the edge of the anode surface for detachment.

- At the vertical anode surface a lot of smaller bubbles were formed and detached randomly.

- The coalescence process at the vertical surface happened quite fast, in about 20 ms from initiation of coalescence to the final bubble shape was established.

Thank you for your attention!