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Electrochemically produced hydrogen bubble probes for gas evolution kinetics and force spectroscopy

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ABSTRACT

The development and characterisation of electrochemically generated hydrogen bubbles for gas evolution kinetics and force spectroscopy are described. Bubbles have been grown at the platinised tip of a commercially available atomic force microscopy (AFM) needle probe (exposed electrode radius $r < 300$ nm) and monitored by CCD camera. Results show consistent bubble growth in galvanostatic conditions. The utility of the bubble probes in AFM force spectroscopy is demonstrated.

1. Introduction

Understanding the fundamental mechanisms governing gas bubble evolution and gas bubbles interactions in fluids has remarkable implications in fields ranging from hydrogen and oxygen production via micro/nanofluidic engineering [1] to biomedical applications [2,3]. Recent advancements in nanofabrication and scanning probe microscopy techniques have created the premises to stimulate the design of experiments aimed at unravelling essential answers to questions regarding gas–solid and gas–fluid–gas interfaces [4–7]. However, so far, the production and manipulation of gas bubbles in fluids were restricted to bubble sizes of several tens of micrometres in radius and for force measurements bubbles were ultrasonically preformed and collected on the hydrophobic side of a cantilever probe [6] or generated by gas injection through needles [8].

Electrochemical gas bubble, i.e. H_2 and O_2, evolution in water electrolysis, involving micrometre and millimetre scale electrodes has been the subject of extensive theoretical [9,10] and experimental studies [11–15]. Gas bubble interactions with solid surfaces [4–6,8,16] had been intensively investigated over the last decade leading to a theoretical framework capable of describing interactions for bubbles with diameters over 100 μm.

Here we report the methodology of electrochemical hydrogen gas bubbles formation by water electrolysis at a platinised nano-electrode and the use of this setup for bubble probe microscopy on the platform of a commercially available atomic force microscope. This methodology is capable of enabling bubble growth with controlled size in the micrometre domain that shall favour a better understanding of electrochemical gas production and gas diffusion dynamics in future. The versatility and simplicity of the method clearly point to its future use in force spectroscopy. We also show the first results of micrometre-sized hydrogen gas bubble interaction dynamics during approach and retraction to/from a glass substrate as proof of this setup suitability for gas/solid interaction force measurements.

2. Experimental

2.1. Instrumentation

Galvanostatic electrolysis has been performed using a DC current source (Keithley 6220, Scientific Devices, Australia). Interaction force measurements were done employing a Nanowizard II Atomic Force Microscope (AFM) (JPK, Germany) equipped with a CellHesion module, which allowed piezo movement in vertical direction up to 100 μm. Glass coverslips of 0.17 μm thickness (Coverglass No. 1, Proscitech, Australia) were used as substrate for AFM measurements after being thoroughly cleaned. TCP (Techno Plastic Products, Germany) dishes were used as electrolysis vessels mounted on the Petri Dish Heater (JPK, Germany) module to control fluid temperature. A platinum wire (radius

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of 1 mm, length of 6 cm) was used as counter electrode. A CCD camera (30 fps, Jenoptik ProgRess, SciTech, Australia) was used for image acquisition. Bubble evolution movies have been processed frame by frame using Nikon NIS Elements (LSE Pty, Australia).

2.2. Probe development

Parylene encapsulated needle probes (NN-EENp-CM28) were purchased from NaugaNeedles (Louisville, KY, USA), with the following specifications: 225 µm cantilever length, 0.6 N m^{-1} spring constant, 28 kHz nominal resonance frequency, 4–12 µm needle length, 100 ± 50 nm exposed needle diameter, and 200 ± 50 nm thick parylene coating. The in-house coating procedure is presented hereafter and uses elements previously reported elsewhere [17]. A silver gallium (Ag_2Ga) nanoneedle is grown on a standard AFM cantilever previously coated by gold to provide electrical contact. Then the cantilever is glued (using conductive glue) to a copper clad chip with an electrode etched in the middle of the chip. The entire device is coated with a 200–400 nm layer of parylene C. Later, the entire device (except the cantilever) is coated by an insulation resin (Red Glyptal, GC Electronics Products, USA). Subsequently, the tip of the nanoneedle is exposed by a proprietary method (performed by NaugaNeedles). Finally, the exposed tip undergoes an electroless platinum deposition stage by immersing it into a 10 mM K_2PtCl_4 solution for 5 to 10 s. Fig. 1 presents the experimental setup: cathode, platinum electrode, reference electrode and AFM probe chip placed on the side in the dish so that the camera beneath captures the profile of the bubble (A), a bubble image capture (B) and schematic of probe cross-section (C).

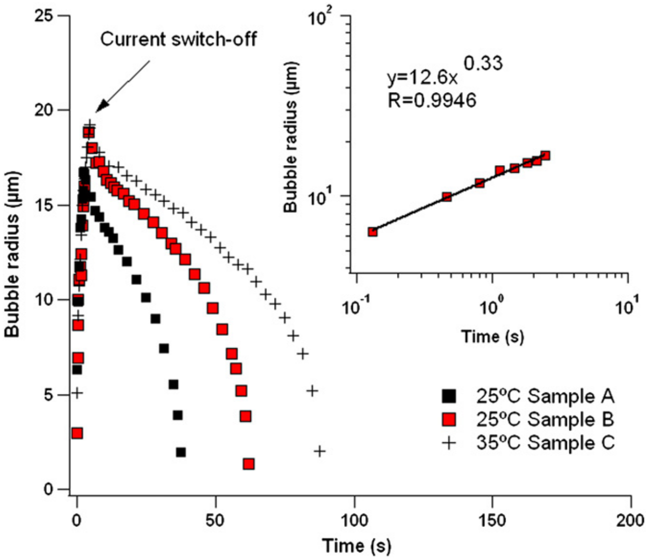

Fig. 2. Typical hydrogen bubble evolution during galvanostatic water electrolysis at 310 nA. After rapid bubble growth during electrolysis, the radius decays when no electrolysis takes place (see arrows). For Sample A current was stopped at 17 µm bubble radius. For Samples B and C current was stopped at 19 µm bubble radius. The inset shows bubble growth data for Sample B at 25 °C consistent with the model from Eq. (1).

3. Results and discussion

3.1. Electrochemical hydrogen bubble evolution

Evolution of single hydrogen bubbles was studied at nano-Pt electrodes, by galvanostatic electrolysis using the nanotip as cathode. Electrolysis was performed in ultra pure water (Milli-Q, resistivity > 18.2 Ω cm) at different temperatures and currents ranging from 60 nA to 500 nA (the voltage on the tip was shown to be always about − 1.8 V (vs. Ag/AgCl) using a WPI, DRYREF, reference electrode, Fig. 1). We chose ultrapure water in order to avoid the cross-reaction of impurities (from electrolytes) at the electrode tip and as occurring potential gradients did not disturb galvanostatic operation. The size of the hydrogen bubble was captured by the CCD camera in side view of the needle. Fig. 2 shows a reduced number of points (for clarity) obtained for the same probe at 25 °C (Samples A and B) and 35 °C (Sample C).

Obviously, during electrolytic bubble growth, two effects will counterbalance each other: i) the faradaic bubble formation, according to $2H^+ + 2e^- \rightarrow H_2$, and ii) the bubble shrinking due to diffusion of H_2 across the liquid/gas interface; both effects result in a dynamic equilibrium: the observable bubble growth. As previously reported [13,14], this bubble growth can be empirically modelled by:

$$r(t) = \beta \cdot t^x \qquad (1)$$

where β is the "growth coefficient" and x is the "time coefficient." Depending on the time, x can be either 0.5, in the case of diffusion control, when $t < 100$ ms, and 0.3 in the stage of faradaic growth,

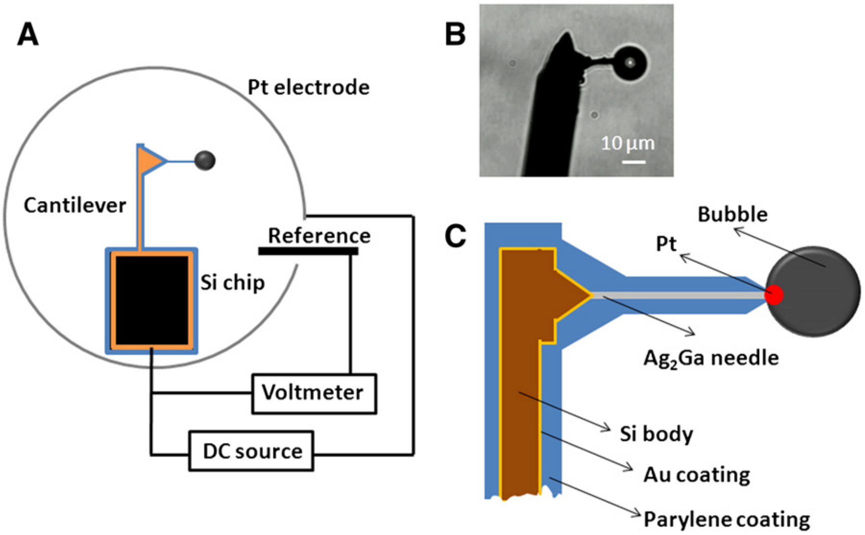

Fig. 1. Bubble probe generation setup (A), photograph of an H_2 bubble probe (B) and probe schematic (C).