The lifetimes of individual H₂ and N₂ nanobubbles, electrochemically generated at Pt nanoelectrodes (7–85 nm-radius), have been measured using a fast-scan electrochemical technique. To measure lifetime, a stable single H₂ or N₂ bubble is first generated by reducing protons or oxidizing hydrazine, respectively, at the Pt nanoelectrode. The electrode potential is then rapidly stepped (<100 μs) to a value where the bubble is unstable and begins to dissolve by gas molecule transfer across the gas/water interface and diffusion. The electrode potential is immediately scanned back to values where the bubble was initially stable. Depending on the rate of this second voltammetric scan, the initial bubble may or may not have time to dissolve, as is readily determined by the characteristic voltammetric signature corresponding to the nucleation of a new bubble. The transition between these regimes is used to determine the bubble’s lifetime. The results indicate that dissolution of a H₂ or N₂ nanobubble is, in part, limited by the transfer of molecules across the gas/water interface. A theoretical expression describing mixed diffusion/kinetic control is presented and fit to the experimental data to obtain an interfacial gas transfer rate of ~10⁻⁹ mol N⁻¹ s⁻¹.

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Electronic interfacial nanobubbles are gaseous, nanoscale spherical caps on a solid substrate immersed in a gas-saturated solution. They were first proposed to explain the long-range attractive interactions between hydrophobic surfaces.1–3 Initially their existence was contentiously debated,4,5 but their existence, composition and stability has since been documented in numerous experiments.6–10 The argument against their existence is due to the lack of a theoretical understanding of their peculiar longevity, often measured in days.11

It is well understood that a spherical bubble suspended in a gas-saturated liquid should be intrinsically unstable. The internal pressure within a bubble of radius R exceeds that of its surroundings by the Laplace pressure, 2γ/w, where γ is the liquid’s surface tension. The gas within the bubble therefore has a higher chemical potential than the dissolved gas and must reach equilibrium by dissolution into the liquid and transport away from the bubble. While this process is quite slow for macroscopic bubbles, the rate of dissolution increases by orders of magnitude for nanoscopic bubbles, due to the increase in Laplace pressure and decreased diffusion lengths. Epstein and Plesset12 first detailed a theoretical framework for growing and shrinking bubbles and later Ljunggren and Eriksson13 explicitly extended the theory to the nanoscale. Both mathematical approaches predict isolated, spherical bubbles smaller than 100 nm radius to dissolve in less than 100 microseconds. Experimentally, and as noted above, nanobubbles are observed to persist for much longer periods, often for several days.11

Several different mechanisms have been proposed to explain the persistence of nanobubbles on surfaces: a transport barrier and lowering of the surface tension by contaminants with an affinity for the gas/water interface,14 a dynamic equilibrium afforded by a recirculating flow above nanobubbles that keeps dissolved gas localized,15 and a thin layer of gas adsorbed to the substrate that feeds into the bubble’s contact line.16,17 Another theory gaining acceptance arises from the experimental observation that the contact radius of a nanobubble may be pinned to the substrate and only the bubble’s height decreases as the bubble dissolves.18 Pinning provides a negative feedback for dissolution, as the Laplace pressure reduces as the bubble shrinks in height and increases its radius of curvature. Mathematical treatment of this model has been presented that suggests pinned bubbles can be stable under a modest gas supersaturation, but will dissolve quite quickly at any level equal to or below saturation.19,20 Indeed, it has been demonstrated that interfacial nanobubbles will dissolve if the solution is degassed,21,22 although experimental measurements of dissolution rates in this situation are lacking. Dissolution rates of micron-sized bubbles in bulk solution have been measured and agree well with the theory of Epstein and Plesset.23,24 However, recent studies of very high curvature nanobubbles by transmission electron microscopy (TEM), where 10-nm radius bubbles were observed to be stable over many seconds, may suggest very different dissolution rates for nanobubbles.25

Electrochemistry provides an interesting avenue for the study of both the nucleation and stability of nanobubbles. Gas producing reactions create large supersaturations near an electrode surface leading to heterogeneous nucleation of bubbles. The resulting ensembles of bubbles decorating electrode surfaces have been imaged by optical microscopy and AFM.26–28 As depicted in Scheme 1, our lab has utilized Pt nanodisk electrodes to generate individual nanobubbles whose size is determined by the size of the electrode. We have reported the generation of individual H₂ bubbles by reduction of protons29,30 (2H⁺ + 2e⁻ → H₂), O₂ nanobubbles by oxidation of water (2H₂O → O₂ + 4H⁺ + 4e⁻),31 and N₂ bubbles by oxidation of hydrazine (N₂H₄ + 4H⁺ + 4OH⁻ → N₂ + 4H₂O + 4e⁻).32 We have demonstrated that the nucleation of a bubble occurs when a critical gas supersaturation

Scheme 1. Schematic drawing of the electrochemical formation of single H₂ and N₂ bubbles from H⁺ electroreduction and N₂H₄ electrooxidation at Pt nanodisk electrodes with radii less than 100 nm.
(310 times saturation for H₂ (0.25 M) and 160 times saturation for N₂ (0.11 M)) is generated at the electrode surface. Once formed, these nanobubbles quickly grow across the electrode surface and reach a dynamic equilibrium, where the diffusive flux of gas out of the bubble is balanced by the electrogeneration of hydrogen, oxygen or nitrogen that enters the bubble, resulting in a stable nanobubble, as shown in Scheme 1.

In this work, we utilize the high temporal resolution of nanoelectrodes to experimentally measure the lifetime of electrochemically generated nanobubbles using a new fast-scan voltammetric method. These experiments represent a crucial test for existing theories regarding the mechanism of nanobubble stability.

Experimental

Sulfuric acid (Mallinckrodt, 96.2%, ACS grade) and N₂H₄ (Aldrich, 35 wt% in water, stored under N₂) were used as received. All aqueous solutions were prepared from deionized water (18.2 MΩ·cm).

Pt nanodisk electrodes were fabricated according to previously reported procedures from our laboratory. The radii of the nanodisk electrodes, a, were determined from the voltammetric steady-state diffusion-limited current, iₘₚ, for the oxidation of ferrocene (Fc → Fc⁺ + e⁻) dissolved in acetonitrile (CH₃CN) containing 0.10 M tetra-butylammonium hexafluorophosphate (TBAPF₆). The radii were calculated using the equation

\[ iₘₚ = 4naF Dₑ Cₑ \]  

where \( Dₑ \) (2.4 × 10⁻⁵ cm²/s) and \( Cₑ \) (3.25 mM) are the diffusion coefficient and the bulk concentration of Fc, respectively, \( n \) is the number of electrons transferred per molecule (\( = 1 \) for Fc oxidation) and \( F \) = 96485 C/mol is Faraday’s constant.

A HEKA EPC10-USB patch clamp amplifier was used for lifetime measurements with current sampling at 100 kHz and a 10 kHz filter. A Ag/AgCl (3 M NaCl) electrode or a saturated calomel electrode (SCE) was used as the counter/reference electrode in a two-electrode cell configuration.

Results and Discussion

As previously reported, the formation of a single H₂ or N₂ gas nanobubble at a Pt nanodisk electrode (as in Scheme 1) can be observed during the reduction of H⁺ and oxidation of N₂H₄, respectively. Figure 1a shows a typical cyclic voltammogram recorded at a 27 nm radius Pt nanodisk electrode immersed in 0.5 M H₂SO₄. As the voltage is scanned to negative potentials, the current associated with H₂ reduction (iₑ₋ₑ⁺) increases rapidly until reaching a peak current, \( iₘₚ,H₂ \), at 23 nA and then suddenly drops to a low residual current. Figure 1b shows a similar peak-shaped cyclic voltammogram for the same 27 nm radius Pt nanodisk electrode immersed in 1.0 M N₂H₄, where the oxidation of N₂H₄ beginning at \( ∼ -0.7 \) V leads to N₂ nanobubble nucleation when the current reaches a value, \( iₘₚ,N₂ \), of 6.5 nA. This characteristic waveshape is due to the formation of a single gas nanobubble at the electrode surface. After formation of a H₂ or N₂ nanobubble, the current decreases to a small residual current, iₚₛₕₕ, which is very stable at potentials negative or positive of the peak potentials for H₂ or for N₂, respectively. As previously reported and detailed, \( iₚₛₕₕ \) corresponds to the rate of H₂ and N₂ electrogeneration at the 3-phase interface (gas/water/Pt, see Scheme 1) that is required to balance the H₂ and N₂ diffusive outflux from the bubble into the bulk solution. H₂ and N₂ nanobubbles are only stable when the electron-transfer reactions are occurring to regenerate the gas lost by dissolution. The low value of \( iₚₛₕₕ \) also indicates that the bubble covers almost the entirety of the electrode. In this work, the radius of the electrode is used to approximate the radius of the bubble at this steady state.

On the voltammetric timescales used in recording the data shown in Figure 1, the bubbles rapidly disappear when the potential is scanned to positive values at the electrode covered by the H₂ bubble, or to negative values for the electrode covered by the N₂ bubble. This is evident by the observations that H₂ oxidation is not visible on the positive-going scan and that the nucleation wave is observed on consecutive voltammetric scans (the high reproducibility of the two consecutive cycles makes it difficult to distinguish them). The peak-shaped waves in Figure 1 would not be observed on the second scans if the bubble persisted on the electrode after electrogeneration of H₂ and N₂ ceased, demonstrating that the bubble fully dissolves during each cycle when the experiment is performed at a scan rate of 200 mV/s.

Kinetics of H₂ and N₂ bubble formation.—Prior to describing voltammetric experiments aimed at measuring nanobubble dissolution rates, we performed a preliminary semi-quantitative investigation of the range of scan rates where nanobubble formation can be observed. Previously, we showed that both the bubble formation and dynamic equilibrium stages are in a steady-state condition as evidenced by the voltammetric waveshapes being insensitive to the scan rate for scan rates less than 2 V/s. At higher scan rates, some distortion of the cyclic voltammograms occurs from capacitive currents and sluggish electron-transfer kinetics. However, it is anticipated that insufficient gas generation and/or the finite rate of bubble nucleation are expected to prevent bubble formation at sufficiently high scan rates. This is born out in the voltammetric data presented in Figure 2, which shows the voltammetric response on the initial forward scan as a function of potential sweep rate. We observe bubble formation at scan rates up to 500 V/s for H₂ reduction and 200 V/s for N₂H₄ oxidation, as evident by the sharp current drop indicating the formation of the gas phase. The increasing overpotential and larger peak currents required for bubble formation suggest that the nucleation step is a relatively slow process, but extracting the kinetics of the phase transformation is complicated by kinetic limitations due to slow electron transfer...
Figure 2. $i-V$ responses for both $\text{H}_2$ and $\text{N}_2$ bubble producing reactions as a function of scan rate at a 32 nm radius nanoelectrode immersed in (a) 0.5 M $\text{H}_2\text{SO}_4$, and (b) 1.0 M $\text{N}_2\text{H}_4$. Bubble formation is observed at scan rates up to 500 V/s for $\text{H}^+$ reduction and 200 V/s for $\text{N}_2\text{H}_4$ oxidation.

(evenly for $\text{N}_2\text{H}_4$ oxidation). While nanobubble formation cannot be observed at scan rates above 500 V/s for $\text{H}_2$ and 200 V/s for $\text{N}_2$, the kinetics for bubble electrogeneration are sufficiently fast to design experiments to measure nanobubble dissolution (vide infra).

**Bubble dissolution rates.**—Figure 3 shows the general strategy and voltammetric waveform used to measure the lifetime of a $\text{H}_2$ nanobubble (an analogous strategy is employed for investigation of $\text{N}_2$ bubble lifetimes). A single $\text{H}_2$ bubble is nucleated (i) by scanning the voltage to negative potentials at a moderate rate (1 V/s), reaching the dynamic steady state (ii) after bubble formation. The voltage is then rapidly stepped (<0.1 ms) to 0 V (iii) and immediately scanned negatively at varying scan rates ranging between 2–500 V/s (iv). There are two experimental outcomes, which can be discriminated by the voltammetric response, and which depend upon the scan rate employed in step (iv). At a sufficiently fast scan rate (iv-b) the $\text{H}_2$ bubble does not completely dissolve, nor is reoxidized (i.e., $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) before hydrogen generation restores the bubble to its steady state at step (v). Conversely, at a sufficiently lower scan rate (iv-a) the $\text{H}_2$ nanobubble has sufficient time to dissolve, or be oxidized, and a new bubble is nucleated on the second forward scan, as the current reestablishes the supersaturation of $\text{H}_2$. As shown in the preceding section, nucleation of a $\text{H}_2$ nanobubble is observed up to 500 V/s. Thus, if the bubble dissolves following the step to the positive potential, the nucleation of a new bubble can be observed on the fast negative-going potential scan.

Figures 4a and 4c show representative $i-t$ traces resulting from the voltammetric experiment schematically depicted in Figure 3, corresponding to the electrogeneration and dissolution of $\text{H}_2$ nanobubbles at (a) 18 and (c) 32 nm radius Pt nanodisk electrodes. An expanded view of the high-speed section of the voltammetric scan is presented in Figures 4b and 4d for each. For each electrode, three different scan rates are shown: two rates slow enough that the bubble dissolves and a faster rate under which the bubble survives. The series of $i-t$ traces in Figure 4a all show the $i_{\text{p}} \sim 13$ nA peak current at $\sim 1.3$ s, denoting the formation of the initial 18-nm radius bubble as the voltage is scanned at 1 V/s to $-1$ V. At 1.81 s, the potential is stepped back to 0.0 V, and scanned to negative potentials again, using different scan rates to determine if the bubble persists or dissolves.

Figure 3. (a) Schematic of the voltammetric experiment used to measure the lifetime of a $\text{H}_2$ nanobubble. The voltage is initially scanned toward negative potentials at 1 V/s resulting in the electrogeneration of $\text{H}_2$ and nucleation (i) of a nanobubble that grows and reaches a dynamic equilibrium (ii). Steps (i) and (ii) result in a voltammetric wave in which the current drops suddenly upon nanobubble formation, as previously shown in Figure 1. At the end of the potential scan (−1 V), the electrode potential is stepped back to 0.0 V (iii), a potential at which $\text{H}_2$ is no longer generated, and the $\text{H}_2$ within the bubble is either oxidized to $\text{H}^+$ or diffuses into the bulk solution. A second scan to negative potentials is initiated immediately after the potential step (iv). If the scan rate of this second forward scan is sufficiently slow, the nanobubble has time to completely dissolve, resulting in the nucleation and growth of a new nanobubble on the negative scan (iv-a), which is readily discerned by appearance of the characteristic voltammetric peak for nanobubble formation. Conversely, if the scan rate is sufficiently fast, the preexisting nanobubble does not have time to dissolve. In this case, the characteristic voltammetric peak is not observed (iv-b), while still restoring the residual current at step (v). By varying the voltammetric scan rate of the second potential scan (step iv) in repeated experiments, the lifetime of the bubble can be determined. An analogous voltage waveform is used to measure the lifetime of $\text{N}_2$ nanobubbles.
In a completely analogous set of experiments, Figure 5 demonstrates the lifetimes of N₂ bubbles can also be measured. The data in Figure 5 were recorded using the same 32 nm Pt electrode used to generate the H₂ nanobubbles shown in Figures 4c and 4d, and show that the N₂ nanobubble does not dissolve at scan rates at ∼10 V/s and above. Note, in contrast to the H₂ bubble and chemically reversible reduction of H², the oxidation of N₂H₄ is not chemically reversible, i.e., N₂ + 4H₂O + 4e⁻ → N₂H₄ + 4OH⁻ does not occur. Thus, the N₂ bubble disappears only by physical dissolution.

Figure 5 shows our experimentally measured lifetimes as a function of the nanobubble/initial bubble radius (points) alongside predictions of bubble dissolution rates from theoretical models (lines). It is clear that our experimentally measured lifetimes are 2 to 3 orders of magnitude longer than predicted by theory from the literature (solid and dotted lines). Theoretical values were computed both for bubbles that maintain a hemispherical shape during dissolution (as in Epstein and Plesset, dotted lines), and for bubbles that are initially hemispherical but whose contact line is pinned at the circumference of the initial bubble (as in Zhang and Lohse, solid lines). (Mathematical details of these models are given in the Appendix.) In the latter case, the bubble radius of curvature increases and, consequently, its internal pressure decreases as it shrinks in height. Both theoretical models assume that bubble dissolution is limited by diffusion and that the dissolved gas concentration at the bubble interface is always at equilibrium with the bubble’s internal pressure (determined by its time-dependent radius of curvature) as described by Henry’s Law. Assuming a mass balance during bubble dissolution, where the number
of gas molecules leaving the bubble to maintain the surface concentration is compensated by a concomitant change in bubble radius or height by the ideal gas law, allowing calculation of the time for the bubble’s volume to reach ideal gas law. The difference in the assumptions of the two theories yields a prediction of approximately a factor of two slower dissolution for the “negative feedback” model of a pinned bubble relative to the “positive feedback” model of a hemispherical bubble. Both models predict that N2 bubbles will have lifetimes ∼3 times longer than a H2 bubble of the same size based upon the difference in dissolved gas diffusion coefficients (1.9 × 10−3 cm2/s and 4.5 × 10−5 cm2/s for N2 and H2, respectively) and difference in gas solubility (0.69 mM/atm and 0.8 mM/atm for N2 and H2, respectively).

Previous studies of dissolution of suspended spherical micrometer-sized bubbles correspond well with the diffusion-controlled predictions of Epstein and Plesset theory within a factor of 2. However, the dissolution of the electrogendriven nanobubbles might not be expected to be diffusion limited. The flux of dissolved gas away from a nanoscale bubble is several orders of magnitude faster than the micron-sized bubbles, and the high internal pressures further increase the outflux. Our measured slower dissolution rates may indicate that a dissolving nanobubble is limited by the transfer of molecules across the gas/water interface. To assess this hypothesis, we modified Zhang and Lohse’s dissolution model of a pinned bubble by adding a first order rate constant for gas/water interfacial transfer, kf, as the sole free parameter (see Appendix for derivation).

The resulting expression (Equation 2/A14) for bubble height, h, as a function of time, t, is governed by

\[
\frac{dh}{dt} = -4DRT \left( \left( \frac{P_{Ext} + \frac{4h\gamma}{a^2 + h^2}}{k_f} \right) \left( 1 + \frac{4DcakH}{\pi(a^2 + h^2)^2k_f} \right) - c_b \right) \alpha \Phi(\theta) \left( \frac{\pi}{6} h(3a^2 + h^2) \frac{4\gamma(h^2 - a^2)}{(a^2 + h^2)^2} + \left( P_{Ext}(a^2 + h^2) + 4k_H \right) \frac{\pi}{2} \right)^{-1}
\]

which can be solved numerically to give bubble lifetimes (i.e., the time when h = 0). P_{Ext} is the external pressure, k_h is Henry’s constant, D is the diffusion coefficient, R is the gas constant, T is temperature, c_b is the gas concentration in bulk solution far from the bubble, a is the bubble’s lateral radius, and \( \Phi(\theta) \) is a geometric factor for mass transport at a spherical cap (1 \( \leq \Phi(\theta) \leq \pi/2 \)) where \( \theta \) is the contact angle. With this model, a value of \( k_f = 1 \times 10^{-9} \text{ mol N}^{-1} \text{s}^{-1} \) provides the best fit to our experimentally determined lifetimes of H2 bubbles (dashed line, Figure 6). The magnitude of this kinetic constant would only have small effects on microbubble dissolution rates, because of the reduction in diffusional fluxes at large size bubbles. While the kinetic fit is not particularly compelling likely due to uncertainties in the experimental setup, our results are intriguing first estimates of interfacial gas transfer limitations at bubbles of nanometer dimensions. To the best of our knowledge, these experiments provide the first direct evaluation of interfacial gas transfer kinetic rates for bubbles less than 100 nm in size.

Conclusions

We have demonstrated a new electrochemical method for the measurement of bubble lifetimes. Studies of H2 and N2 nanobubbles show dissolution rates that are ∼1000 times slower than predictions from extant theories assuming a diffusion-limited process, indicating that the finite rate of gas transfer across the gas/liquid interface limits dissolution for nanobubbles. These experiments represent an extreme test case where the rate of gas transfer across an interface may not be able to maintain the high equilibrium surface concentration due to the exceedingly fast diffusion of dissolved gas away from the bubble’s nanometric gas/water interface. Our results are in closer agreement to these theories than previous observations of interfacial nanobubbles via AFM and TEM. Characterization of the bubble and/or electrode sizes with other imaging techniques may bring our lifetime values in closer agreement with theoretical expectations, or will provide stronger evidence for the development and testing of new theories.

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Appendix

Derivations of analytical expressions for bubble lifetimes.—The following are descriptions of the derivations of expressions used to fit the data in Figure 6 of the main text, as well as the model including interfacial transfer kinetics, Equation 2, described in the discussion of this figure. The assumptions made in deriving these expressions are explicitly stated.

All derivations are founded upon a few similar descriptions. The bubble on a surface is assumed to take the shape of a spherical cap, can be described by a number of different geometric parameters as is shown schematically in Figure A1. Elementary

Figure A1. Schematic showing the geometric parameters describing the geometry of a bubble pinned on a surface.
geometry/trigonometry gives the following interdependencies:

\[ \sin(\theta) = \frac{a}{R} \]  \[ \text{[A1]} \]
\[ R = \frac{a^2 + h^2}{2b} \]  \[ \text{[A2]} \]

The volume of the spherical cap, \( V \), and surface area of the gas/liquid interface, \( A \), are defined by

\[ V = \frac{\pi}{6} h (3a^2 + h^2) \]  \[ \text{[A3]} \]
\[ A = \pi(a^2 + h^2) \]  \[ \text{[A4]} \]

The pressure, \( P \), may be described by the Laplace equation (Equation A5), where Equation A2 may be substituted in for the radius of curvature of the bubble, \( R \)

\[ P = \frac{2\gamma}{R} + P_{Ext} = \frac{4\gamma h}{a^2 + h^2} + P_{Ext} \]  \[ \text{[A5]} \]

\( P_{Ext} \) is the externally applied pressure (1 atm = 101,325 Pa) and \( \gamma \) is the liquid-gas surface tension (0.072 J/m²).

The ideal gas law relates pressure, volume and temperature (\( V = RT \)) to the amount, \( n \) (moles), where \( R = 8.31 \text{ J/(K mol)} \).

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