The corona of a surface bubble promotes electrochemical reactions

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The evolution of gaseous products is a feature common to several electrochemical processes, often resulting in bubbles adhering to the electrode's surface. Adherent bubbles reduce the electrode active area, and are therefore generally treated as electrochemically inert entities. Here, we show that this general assumption does not hold for gas bubbles masking anodes operating in water. By means of imaging electrochemiluminescent systems, and by studying the anisotropy of polymer growth around bubbles, we demonstrate that gas cavities adhering to an electrode surface initiate the oxidation of water-soluble species more effectively than electrode areas free of bubbles. The corona of a bubble accumulates hydroxide anions, unbalanced by cations, a phenomenon which causes the oxidation of hydroxide ions to hydroxyl radicals to occur at potentials at least 0.7 V below redox tabled values. The downhill shift of the hydroxide oxidation at the corona of the bubble is likely to be a general mechanism involved in the initiation of heterogeneous electrochemical reactions in water, and could be harnessed in chemical synthesis.
Major industrial processes, such as the electrolysis of alumina\(^1\), the chloralkali process\(^2\), and the refining of copper\(^3\), involve the evolution of gases, which are often accompanied by gas bubbles forming at the electrode. An adherent bubble masks a portion of the electrode; it resists the passage of electrical currents by disrupting ionic conduction at the solid–liquid interface. Surface gaseous cavities are therefore generally regarded as undesirable and electrochemically inactive entities\(^4\).

The gas–water interface is, however, not electrically neutral\(^5\), and the interface between water and gas carries electric fields as high as 1.4 V nm\(^{-1}\)\(^6\)–\(^8\). Measurements of zeta potential for bubbles suspended in ultrapure water indicate that the corona of a bubble is electrified due to the accumulation of hydroxide ions (OH\(^-\))\(^9\). This is most likely caused by the increased self-ionization constant of water at the gas–water interface\(^10\), which coupled to the fast diffusion of protons by the Grotthuss mechanism\(^11\), leaves the water surface with an OH\(^-\) excess. Adhesion of a bubble on a solid surface leads to two interfaces, the solid–gas and the gas–liquid, with the gas obviously acting as an electrically insulating cavity separating the electrode from the liquid\(^4\)\(^12\). However, with an analogy to a suspended gas cavity, at the point where the solid, the gas, and the liquid meet, a high concentration of unbalanced hydroxide ions is likely to exist. We, therefore, postulated that, due to mutual destabilization of hydroxide ions by electrostatic repulsion, the one-electron oxidation of hydroxides to hydroxyls could be significantly facilitated around bubbles adhering to an electrified support. The oxidizing power of hydroxyls (HO\(^+\) + e\(^-\) = OH\(^-\), E\(^0\) = +1.90 V vs. SHE)\(^13\) could then be harvested to trigger redox chemistry\(^14\)\(^15\).

Results
Increase in electrochemical current densities in the presence of adherent bubbles. Starting with a simple experimental setup, current measurements and optical images in Fig. 1a, b show, unambiguously, that adherent oxygen bubbles (Fig. 1c) are not electrochemically inert entities. In an electrolyte solution containing only 0.1 M sodium hydroxide, the anodic current measured at an indium tin oxide (ITO) electrode, biased at +1.2 V vs. SHE, is surprisingly higher in the presence of macroscopic surface-adherent oxygen bubbles than it is in their absence. An increased electrochemical current is observed in the presence of bubbles, regardless of the gas composition (Supplementary Fig. 1), and the electrochemical current systematically increases by increasing the cumulative bubbles’ perimeter (C, Fig. 1a, b, Supplementary Fig. 2, and Supplementary Table 1). Surface static bubbles favor the oxidation of hydroxides to hydroxyls, and this is a surprising result; a small increase in the gas–water interface outbalances the net loss of “wet” electrode area. We note that these macroscopic bubbles are stable over the time frame of the electrochemical measurements (Supplementary Fig. 3); hence, localized changes in redox reactivity are due to characteristics of the gas–water interface, rather than to energy released during the rapid collapse of the cavity, such as in sonochemistry\(^16\)–\(^18\), to convection enhancement\(^19\), or the cavity absorbing dissolved gas products\(^20\).

To confirm that the increase in anodic currents, shown in Fig. 1a, is arising from the oxidation of OH\(^-\) to HO\(^+\) around adherent gas cavities, we coupled electrochemical experiments to epifluorescence microscopy to visually detect the presence of HO\(^+\) in the corona of surface bubbles (Fig. 1d). Figure 1e, f (see also Supplementary Video 1) shows epifluorescence microscopy data of argon bubbles resting on an ITO electrode, with 3’-(p-hydroxyphenyl) fluorescein (HPF) present in the electrolytic solution. When the electrode is biased anodically (+1.2 V vs. SHE), a sharp increase in the fluorescence contrast is observed between the bubble’s surface and electrode regions away from the cavity. In our model system, made up of only sodium hydroxide, water, and gas, the plausible reactive oxygen species augmenting the fluorescence of HPF are HO\(^+\) and H\(_2\)O\(_2\). HPF is ca. 400 times more selective toward HO\(^+\) than to H\(_2\)O\(_2\)\(^3\), strongly suggesting that HO\(^+\) is being generated in the corona of the bubble. Confocal microscopy images, acquired at different z heights over the electrode surface (Fig. 1g, h), show that hydroxyl radicals are generated in proximity of the gas–water interface, but principally at a height close to the electrode substrate (Fig. 1i).

Hydroxyl radicals from the oxidation of hydroxide ions. We note that the increased electrochemical reactivity of surface bubbles observed here is not simply the manifestation of higher current densities observed at regions of an electrode that are partially masked by a dielectric object\(^4\)\(^22\). A local increase in current density implies a reaction rate increase for a favorable reaction, while the oxidation of OH\(^-\) to HO\(^+\) is thermodynamically unfavorable at +1.2 V vs SHE. Instead, the contra-thermodynamic shift experienced by the OH\(^-\) oxidation in the presence of surface-adherent bubbles is more likely linked to the high unbalanced concentration of OH\(^-\) at the gas–liquid interface (Fig. 2a). Based on Nernst considerations, the HO\(^+\)/HO\(^-\) redox potential, +1.9 V at standard conditions\(^13\), will drop only by 59 mV every order of magnitude in increase in OH\(^-\) activity (Fig. 2b, dashed line). However, if largely unbalanced by cations, electrostatic repulsions between adjacent OH\(^-\) are likely to further lower their oxidation potential, as demonstrated by our quantum-chemical simulations (Fig. 2b, symbols, and Supplementary Note 1). It was, therefore, necessary to first estimate experimentally the OH\(^-\) excess concentration at the gas–water interface of bubbles. This excess was first determined by means of accelerating gas bubbles, suspended in ultrapure water, under an electric field (Supplementary Note 2)\(^9\). Selected video frames (Supplementary Video 2), reproduced in Fig. 2c, show a microscopic (50 µm) oxygen bubble in ultrapure water moving at a velocity of 1.3 mm s\(^{-1}\) toward the anode under a field of ca. 40 V cm\(^{-1}\). Similar results were obtained for nitrogen bubbles suspended in water (Supplementary Fig. 4 and Supplementary Video 3). The gas–water interface carries an unbalanced population of OH\(^-\), causing the electrical potential to drop away from the gas–liquid interface (Fig. 2a). A quantitative descriptor of this potential profile is the bubble’s zeta potential \(\zeta\) that, is the potential difference between the shear plane and the bulk solution\(^13\). We obtained a \(\zeta\) value of –526 ± 138 mV from the measured bubble velocities using the Smoluchowski equation\(^24\). The surface charge density of a spherical particle relates to \(\zeta\) and using the relationship proposed by Loeb et al\(^25\), we estimated a charge density of –52 µC cm\(^{-2}\) or the equivalent of 5.4 × 10\(^{-10}\) mol cm\(^{-2}\) of OH\(^-\). To confirm that the negative charge of bubbles is linked to a local unbalanced excess of hydroxide ions, we resorted to direct pH measurements of gas/water emulsions (Fig. 2d). These experiments have strong conceptual analogies with the “pH-stat” experiments reported by Beattie and coworkers for oil emulsions in water\(^26\). Suspensions of fine nitrogen bubbles are a way to access a water sample characterized by the presence of a very large gas–liquid interface, and as such, a drop in pH would be expected if an excess of OH\(^-\) is trapped at the interface of water with the gas. By generating a large concentration of microscopic nitrogen bubbles (9.3 × 10\(^7\) particles L\(^{-1}\), Supplementary Video 4) in a water sample, such pH drop was in fact observed (Fig. 2e), indicating at pH ~7 (quiescent sample) a surface OH\(^-\) excess of 4.2 × 10\(^{-11}\) mol cm\(^{-2}\) (Supplementary Note 3). At pH ~12, such as where hydroxyl radicals are detected (Fig. 1), this excess rises to 1.3 × 10\(^{-7}\) mol cm\(^{-2}\) (Supplementary Fig. 5).
The current measurements reported in (bright-field image (side view) of an oxygen bubble on the ITO electrode. The scale bar is 200 µm.) and sodium hydroxide (0.1 M). The z height above the electrode surface is specified in the figure. Scale bars in e-h are 200 µm. Emission intensities for the images (frames) in e-h are normalized to the highest-intensity value measured in each frame. i Fluorescence emission intensity profiles measured along the dashed lines of panels g, h, showing a larger emission at the gas-liquid interface closer to the electrode surface.

Anisotropic polymerization of luminol around surface bubbles. To demonstrate the scope and extent to which the surface of an adherent bubble enhances the oxidizing power of an electrode, we designed a detection scheme capable of imaging in real-time the 2D growth of a polymer around bubbles. We coupled an electrochemiluminescent reaction with a step polymerization, linking neighboring bubbles rather than growing radially from the bubble. The luminol light path in water begins with the oxidation of the luminol monoanion31, yielding a radical susceptible to nucleophilic attack by superoxide (O2•−). This intermediate collapses to a light-emitter excited state of 3-(p-hydroxyphenyl) fluorescein (10 µM), and it is either rested at its open-circuit potential (OCP), or biased at +1.2 V vs. SHE (f). See also Supplementary Video 1. g, h Confocal microscopy images for the HO• detection around nitrogen bubbles supported on a biased (+1.2 V vs. SHE) ITO slider. The aqueous electrolyte contains dichlorodihydrofluorescein diacetate (100 µM) and sodium hydroxide (0.1 M). The z height above the electrode surface is specified in the figure. Scale bars in e-h are 200 µm. Emission intensities for the images (frames) in e-h are normalized to the highest-intensity value measured in each frame. i Fluorescence emission intensity profiles measured along the dashed lines of panels g, h, showing a larger emission at the gas-liquid interface closer to the electrode surface.
considering electrostatic repulsions between OH
initiated via hydrogen transfer by the HO
by generating a high quantity of nitrogen microbubbles (9.3 × 10⁷ L
drop induced by the formation of a gas emulsion in water.

imaging experiments (Supplementary Video 2), tracking the position of an oxygen bubble accelerating in ultrapure water toward the anode under an
electric field of ca. 40 V cm⁻¹. Scale bars are 500 µm. d Photographs taken prior (left) and after (right) the formation of a fine gas-water emulsion obtained
by generating a high quantity of nitrogen microbubbles (9.3 × 10⁷ L⁻¹, average bubble diameter is 50 µm), see Supplementary Note 3. e Representative pH drop induced by the formation of a gas emulsion in water.

Supplementary Fig. 7) also reveal that the reach of the oxygen radicals away from the bubbles’ surface is dramatically increased when peroxide is present, reflecting the million-fold increase in lifetime for O₂⁻ over HO²⁻. The oxygen radical gradient around bubbles is schematized as a color map in Fig. 3c. Bubbles continuously grow as a result of oxygen-evolving upon the oxidation of HO₂⁻, and they will occasionally collapse or detach (Fig. 3b and Supplementary Video 7).

The chemiluminescence emission is higher at the bubble interface than on the electrode surface, Fig. 3a, as expected from a higher concentration of HO²⁻ around bubbles (from OH⁻ oxidation) that react with HO₂⁻ to generate O₂⁻. Luminol can be oxidized to its radical electrochemically (Supplementary Fig. 8), and/or by HO²⁻ and O₂⁻ forms when HO²⁻ oxidizes HO₂⁻. The latter has to be present in order to observe chemiluminescence. Therefore, both luminol and HO₂⁻ might compete for HO²⁻, which would make the emission intensity reach a maximum value at a specific HO₂⁻/luminol ratio, and then decrease as this ratio further increases, as was effectively observed (Fig. 3d).

The polymerization reaction starts at the bubble interface from the free oxygen radical attack to luminol (Supplementary Note 6). XPS analysis indicates that multiple pathways are operative, with a film curiously consisting of 50% polyaminophthalate, and 50% of polyaminophthalazine and/or polyluminol (Supplementary Note 4). Theoretical calculations suggest that the polymerization mechanism is a stepwise radical process in which a “step” is first initiated via hydrogen transfer by the HO²⁻ radical from aniline functionality of the monomer (Fig. 3e and Supplementary Note 6). Two such resulting radicals couple to form an intermediate that then undergoes a second hydrogen transfer followed by coupling with the radical of a further monomer unit to regenerate the active end group in its nonradical form. In total, three monomer units are joined per step, and four molecules of HO₂⁻ are consumed. Calculations show that the pathway is feasible for all monomers and hence copolymerization is likely.

Figure 3f (solid line) shows the experimental amperometric curve (electrochemical current vs. time) for the polymerization reaction, with a characteristic shape of an electrodeposition process, confirming that the electrode acts as an electron sink rather than being a homogeneous redox reaction. The electrochemical current goes through a rapid initial increase due to the formation and growth of independent nuclei under hemispherical diffusion control. When these diffusion fronts overlap, as a result of a small separation between nuclei, the overall current reaches a maximum and then starts to decrease. The experimental amperometric curves show a good fitting for a diffusion-limited nucleation growth. The initial exponential decay is due to the oxidation of the adsorbed polymer, and this process was accounted for in the fitting as an additional component over the diffusion-limited instantaneous nucleation, see Supplementary Note 7. The peak maxima observed in Fig. 3f represent the point in time at which diffusion fronts theoretically overlap (tₘₐₓ), and roughly coincide with the point in Fig. 3a when the polymer films growing between bubbles start overlapping (t = 13 s).

Our results demonstrate that at anodes operating in the water, surface static bubbles are not inert cavities but rather highly reactive redox sites. The electrochemical reactivity of an adherent bubble originates from its corona’s ability to accumulate an
unbalanced excess of hydroxide anions. In the proximity of the electrode surface, unbalanced anions are oxidized to highly reactive hydroxyl radicals at potentials as low as $+1.2$ V vs. SHE. The gradient of reactive oxygen species surrounding adherent bubbles can affect anisotropic oxidative redox chemistry. The results presented here are likely to be a general mechanism to initiate, enhance, or localize oxidative processes occurring in water electrolytes.
Methods

Chemicals and materials. Unless specified otherwise, all chemicals were of analytical grade and used as received. Hydrogen peroxide (H₂O₂, MOX Paranal, 30%, Sigma Aldrich), 3-(p-hydroxyphenyl) fluorescein (HPF, 5 mM solution in NN-dimethylformamide, DMF, ThermoFisher), dimethyl sulfoxide (DMSO, 99%, Ajax Fisher), sodium hydride (NaOH, Sigma Aldrich), sulfuric acid (H₂SO₄, 97%, Scharlab), monosodium phosphate (NaH₂PO₄, 99%, Sigma Aldrich), oxygen (O₂, 99.95%, Coregas), nitrogen (N₂, 99.9%, Coregas), and argon (Ar, 99.997%, Coregas) were used as received. Milli-Q water (>18 MΩ cm) was used for surface cleaning procedures and for preparing all solutions. ITO-coated glass slides were purchased from Delta Technologies (8–12 Q/s in sheet resistance).

Measurements of the zeta potential of bubbles. To measure the zeta potential of suspended microscopic oxygen and nitrogen bubbles (50 µm in diameter), we used a method based on the procedure of Takahashi. In brief, oxygen or nitrogen gas was bubbled for 1.5 h across an ultrapure water sample held inside a frift-free soda-lime glass cell (see Supplementary Fig. 9). The cell consisted of two vertical arms of 10 cm in length connected by a horizontal arm 4 cm long. All arms had an internal diameter of 1 cm. A gas dispersion tube of 25–50-µm porosity (Z408743-1EA, Sigma) was used to pass the oxygen or nitrogen gas along with one of the vertical arms. The oxygen or nitrogen flow was stopped, and a bias of 200 V was applied to a high-precision 10 mcA source/measure unit (model B2902A). Between two platinum wire electrodes (99.99% +, 0.5-mm diameter, Goodfellow Cambridge Ltd) inserted in each of the two vertical compartments of the H cell. The bubbles’ movement (speed) in the horizontal channel, and along a horizontal direction pointing from the cathode toward the anode, was used to estimate the bubble zeta potential. Specifically, we calculated the bubble position as a function of time were recorded at 25.13 frames per second, using a CCD camera (DC1240C, Thorlabs) fitted with a 6.5× zoom (MV16X123Z and MV133A, Thorlabs). Video recordings were analyzed frame by frame using Fiji image processing package. To minimize electroosmotic forces, possibly interfering with the bubble migration velocity in the field, the focus of the camera was aimed toward the center of the H-cell horizontal arm. This is to minimize surface-related artifacts on the zeta potential measurement. The 95% confidence interval of the zeta potential means is reported as t−1/2 × s, where t−1/2 depends on the number of repeats, s is the standard deviation, and n is the number of independent measurements (which was 11 for the oxygen bubbles and 23 for the nitrogen bubbles).38

Determination of the OH• excess at the gas-water interface. In addition to quantitative data obtained by electokinetic experiments (Fig. 2c), the excess of OH• at the interface of a gas bubble suspended in water was also estimated from bulk pH changes (Fig. 2e) recorded when forcing large fluxes of microsopic nitrogen (99.9%) bubbles in a water sample (Fig. 2d). These vigorously aerated samples have a large gas-water surface-to-volume ratio, and were cleaned after each measurement by electrochemical cycling (20 cycles at a sweep rate of 0.1 V/s) in 0.5 M aqueous nitric acid and then rinsed with Milli-Q water.

Confocal microscopy. 12-bit fluorescence and differential interference contrast microscopy images at 512 × 512 px resolution were captured using a Nikon A1R laser scanning confocal microscope coupled to a Nikon Ti-E inverted microscope, using a Plan Apo 10×/0.45 objective with excitation set to 488 nm, emission to 525/50 nm, and with a DU4 detector. Images were captured at 1.00x zoom and a pinhole size of 17.9 µm. The electrochemical cell was the same as that used for the epifluorescence and chemiluminescence microscopy experiments.

Composition of H₂O₂ and luminol for HO••. The composition of hydrogen peroxide and luminol for HO•• as their oxidant was studied by chemiluminescence spectroscopy with a Cary Eclipse Fluorescence spectrophotometer, using a spectroelectrochemical cell from BASI (EF-1362) fitted with a platinum gauze as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl/KCl (sat.) as the reference electrode. All electrochemical measurements were performed using a potentiostat from PalmSens BV (EmStat3). All potentials are reported against the SHE. The chemiluminescence intensity was measured at the peak maxima (425 nm) at an applied potential of +1.2 V in a solution containing 5.0 × 10⁻⁴ M luminol, 0.1 M sodium hydroxide, and concentrations of hydrogen peroxide ranging from 1 × 10⁻³ to 0.5 M. The platinum electrode was cleaned after each measurement by electrochemical cycling (20 cycles at a sweep rate of 0.1 V/s) in 0.5 M aqueous nitric acid and then rinsed with Milli-Q water.

X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy was performed with an ESCALab 250 Xi spectrometer (ThermoFisher Scientific) fitted with a monochromated Al Ka source. The pressure in the analysis chamber during measurements was <10⁻⁸ mbar. The pass energy and step size for narrow scans were 20 and 0.1 eV, respectively, and the take-off angle was normal to the sample surface. Spectral analysis was performed by using the Avantage 4.73 software and curve fittings were carried out with a mixture of Gaussian–Lorentzian functions. Emission peaks were calibrated by applying a rigid binding energy shift to bring the Cls emission of the C–C signal to 284.3 eV.

Theoretical procedures. Quantum-chemical calculations were undertaken to assess the possibility of electrostatically driven peroxide homolysis, to determine the effect of charge repulsion on hydroxide oxidation, and to ascertain the mechanism of luminescence polarization. A summary of the methods is given below, further details are provided in the relevant Supplementary Notes.

Calculations on peroxide homolysis and luminescence polarization were carried out with the Gaussian 16 DFT package, 1606/6-31 + G(d,p) level of theory for both geometry optimizations and frequency calculations. Where relevant, conformational searching was also carried out at this level using the energy-directed tree search algorithm. For peroxide homolysis, a thermocycle approach was used to obtain aequous-phase Gibbs free energies from gas-phase Gibbs free energies and SMD solvation free energies in the gas and aqueous phases were significantly different, and so the direct method was used instead. In both cases, standard partition functions for an ideal gas under the harmonic oscillator- rigid rotor approximation were used. For peroxide homolysis, the electric field was applied using the field command in Gaussian at field strengths of 2 and 10 V/Å, with atomic units, the field was applied to the closest field at the bubble surface. Multiple directions were screened and the most stabilizing directions applied in all cases.
To assess the effects of charge repulsion on hydroxide oxidation, a 1 M solvent system comprising 1 hydroxide and 52 water molecules was extracted from the trajectory of a 1 ns NVT simulation of a system containing 1 hydroxide and 100 water molecules in cubic boxes with a length of 14.46 angstrom based on the density of water. The initial cubic box was set up using the Packmol program and the Travis program was used to place a solute molecule (HO\(^-\) or HO\(^-\)) in the center of each simulation box. For each cluster, the GFN2-xTB method implemented in the xtb program (version 6.2.3) was used to optimize the structure, and the most stable cluster is taken for further optimization using the B97-3c method with the ORCA program. Improved energies were calculated with RI-PWPB95-D3(BJ)[45,54] def2-QZVPP\(^2\) single-point energies and these were further corrected to an absolute level via an ONIOM approximation\(^2\) in which the core system was the isolated reagent. Oxidation potentials were computed using a value of 4.281\(\text{V}^{\text{th}}\) for the reference electrode and Boltzmann statistics for the electron. The effect of electrostatic repulsion was assessed by repeating the calculations for simulation boxes in which 1 (2 M) or 2 (3 M) extra HO\(^-\) ions were included.

**Data availability**

Data supporting the findings of this work are available within the paper and its Supplementary Information documents. The optimized coordinates for the HO\(^-\) and HO\(^-\) systems are deposited at https://figshare.com/s/5a74a21f8da297e73.

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Author contributions

Y.B.V. and S.C. conceived the study. Y.B.V. performed most of the experiments, carried out the analysis, and produced the figures. C.W.E. assisted with the microscopy experiments. M.B. performed the electrokinetic experiments. L.X. studied the effect of HO• repulsion on oxidation. M.L.C., I.C.R., L.J.Y., and A.K.K.F. determined the polymerization mechanism. I.C.R. and N.S.H. evaluated peroxide homolysis as an alternative source of HO•. V.R.G. performed the XPS experiments. N.D., M.L.C., K.S.I., and S.C. supervised the project. Y.B.V. and S.C. wrote the paper with contributions from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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