Modelling of surface nanobubbles in electrochemical gas evolution reactions

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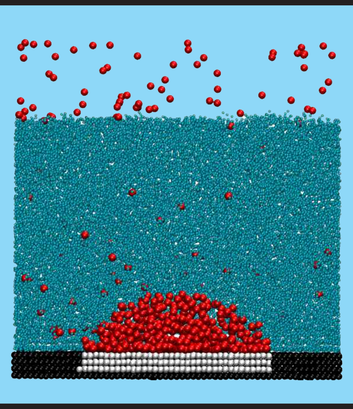
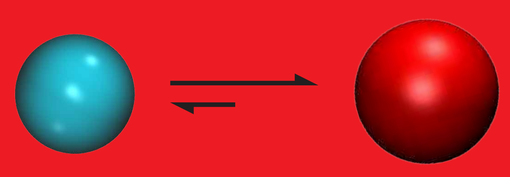


The study of **surface gas bubbles** using nanoelectrodes allowed the **electrogeneration of individual nanobubbles** of H_2, O_2 and N_2 on Pt nanodisks of radii ranging from 2.5 nm to 90 nm[1]. After nanobubble nucleation the system reaches a dynamic equilibrium state where the value for the **residual current** does not depend on the applied voltage. This stationary state is obtained by a compensation between the diffusional gas outflux and the electrochemical production of gas. In our recent work, Molecular Dynamics simulations showed an unexpected observation: despite **invariance of the residual current** with the applied potential **the size and shape of the nanobubble did not remain constant** as the driving force increased.

The MD-kMC scheme

The simulation procedes alternating MD and kMC steps. During each MD step positions and velocities are updated. We used the coarse grainded mW[2] model for water and a single particle gas representation. The kMC is responsable for the simulation of the electron transfer events.



1 electron process

For each new set of positions the kMC algorithm computes the reaction probabilities according to the individual reaction rates k_f

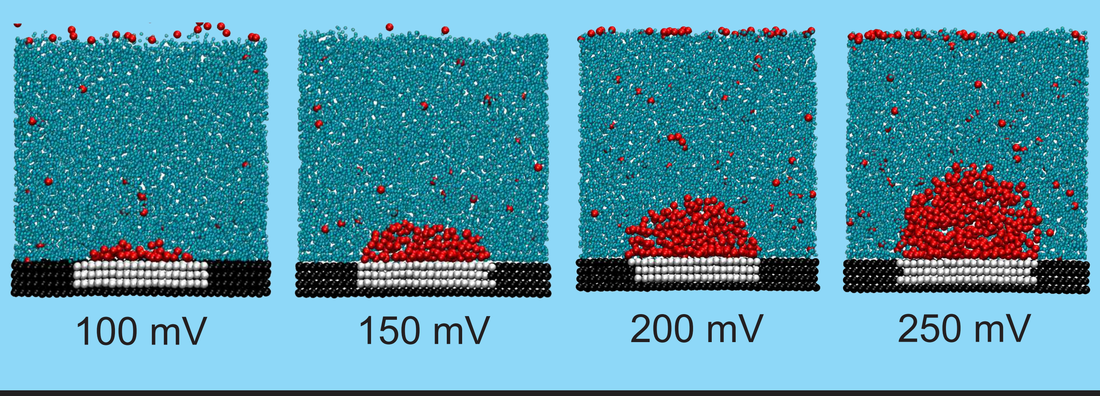
$$P_f = 1 - exp(-k_f \tau)$$

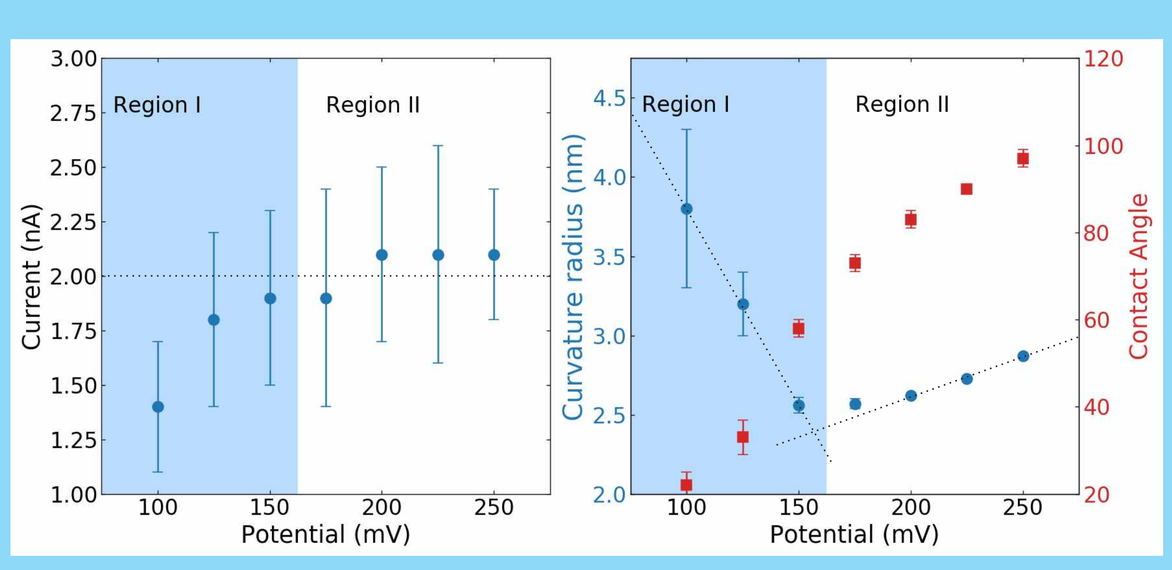
Each molecule in the proximity of the electrode has a k_f value wich depends on the applied potential (E) according to Marcus first order kinetics[3]

$$k_f = k_0\, exp(-\beta r)\, exp\left[\frac{(1-\alpha)nF}{RT}(E - E^0)\right]$$

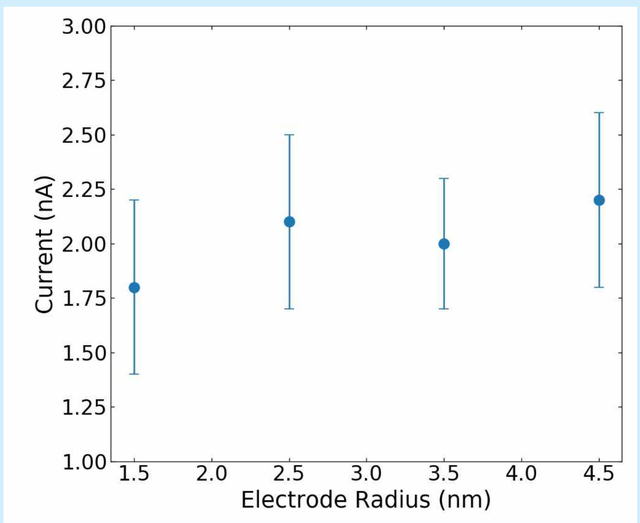
Results

The shape and current dependence with the applied potential presents **two regions.** The region above 175mV presents a **constant current value** comparable with the experimental current for the same electrode size.





The steady state current does not seem to be sensitive to the lenght of the three-phase contact line between the 1.5 nm and the 4.5 nm electrodes. Thus, it is unlikely that the current is determined by the gas production.



These results support the hypotesis that the **nanobubbles from different potentials and electrode sizes have a similar diffusional gas outflux.**

The equation for the total mass outflux (dW/dt) from the bubble in the quasistatic limit is

$$\frac{dW}{dt} = -4\pi D R (C_R - C_\infty) f(\theta)$$

For curavture radii under the micrometer scale the Laplace pressure dominates the internal pressure of the bubble, and assuming that the concentration at the nanobubble's surface is determined by Henry's law

$$\frac{dW}{dt} = \frac{-8\pi D\sigma}{K_H} f(\theta)$$

The magnitud of dW/dt becomes independent to the curvature radius, but the geometric factor (*f(ɵ)*) still affects the total mass outflux.

References

[1]Langmuir, 2013, 29 (35), pp 11169–11175

[2]J. Phys. Chem. B, 2009, 113 (13), pp 4008–4016

[3]Langmuir, 2008, 24 (6), pp 2850–2855

-The size of the nanobubble (and thus the electrode coverage) adjusts until the electrochemical gas production balances the diffusional outflux.

-Different nanobubbles present almost negligible difference in their gas outflux, ultimately producing a constant residual current value.