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Potential drops due to an attached bubble on a gas-evolving electrode*

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It is shown how the various components of the overpotential due to an attached bubble on an electrode can be separated and estimated. By considering the resistance increments due to the presence on the electrode surface of a bubble, obtained from impedance measurements, it is possible to determine the predominant potential distribution which controls the gas evolution. A relationship between the measured overpotential and the diameter of the bubble is established. The time evolution of the overpotential due to a growing bubble is modelled in the case of the limitation of the bubble growth by dissolved gas diffusion in the solution. In agreement with previous experimental results a linear time variation is found.

Nomenclature

b_b, b_f	Tafel coefficients (V^{-1}) Equation A7
δc	difference between the supersaturation and saturation concentrations ($mol\,m^{-3}$)
C	electrode double layer capacity (F)
C_0	electrode double layer capacity per surface unit ($F\,m^{-2}$)
C_A, C_B	concentrations of species A and B in the redox system ($mol\,m^{-3}$)
d_b	diameter of a bubble or a sphere on the electrode (m)
d_e	diameter of the disc electrode (m)
D	diffusion coefficient of the dissolved gas ($m^2\,s^{-1}$)
E	electrode potential (V)
E_z	zero-charge potential of the electrode (V)
F	Faraday constant, $=96487\,C\,mol^{-1}$
I	electrolysis current (A)
I_F	faradaic current (A)
k_b, k_f	heterogeneous rate constants of the redox reaction ($m\,s^{-1}$)
k_1	slope of $\Delta V/t$ curve ($V\,s^{-1}$), Equation 5
k_2	slope of $\Delta V/t^{2/3}$ curve ($V\,s^{-2/3}$), Equation 5
K	Henry coefficient, Equation 1
n	number of the electrons involved in the reaction to form one molecule of the dissolved gas
Q	electrical charge of the electrode double layer (C)
r_b	radius of a bubble or of a sphere on the electrode (m)
R_e	electrolyte resistance (Ω)
R_{e0}	electrolyte resistance for an electrode of 1 m in diameter (Ωm), Equation 32
R_p	polarization resistance (Ω)
R_{p0}	polarization resistance per surface unit ($\Omega\,m^{-2}$)
R_t	charge-transfer resistance (Ω)
s	relative rate of variation of the electrode active surface due to a growing bubble (s^{-1})
S	disk electrode surface (m^2)
ΔS_e, ΔS_p	equivalent screened surfaces by a bubble or a sphere given by R_e and R_p changes (m^2), Equations 18 and 29
t	time (s)
V	potential difference between the working and the reference electrodes (V)
V_0	gas molar volume: $24.5 \times 10^{-3}\,m^3$ at 298 K
ΔV	total overpotential increment due to a bubble or a sphere (V)
ΔV_a, ΔV_{ohm}	activation and ohmic overpotential increments due to a bubble or a sphere (V)

Greek characters

α	slope of $\log \Delta V/\log I$ curve, Equation 11
α_e, α_p	dimensionless parameters in Equations 27 and 30
β	dimensionless coefficient in Scriven law, Equation 2
η_t	total overpotential (V)
η_a, η_c, η_{ohm}	spatial averages of the activation, concentration and ohmic overpotentials over the electrode surface (V)
ϱ	electrolyte density ($kg\,m^{-3}$)

Subscript

i	in the absence of the growing bubble

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