

Investigation of water electrolysis by spectral analysis.

I. Influence of the current density*

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The potential (or current) fluctuations observed under current (or potential) control during gas evolution were analysed by spectral analysis. The power spectral densities (psd) of these fluctuations were measured for hydrogen and oxygen evolution in acid and alkaline solutions at a platinum disk electrode of small diameter. Using a theoretical model, some parameters of the gas evolution were derived from the measured psd of the potential fluctuations, such as the average number of detached bubbles per time unit, the average radius of the detached bubbles and the gas evolution efficiency. The influence of the electrolysis current on these parameters was also investigated. The results of this first attempt at parameter derivation are discussed.

Nomenclature

b	Tafel coefficient (V^{-1}), Equation 46
C	electrode double layer capacity (F)
e	gas evolution efficiency (%)
f	frequency (Hz)
f_p	frequency of the peak in the psd ψ_v and ψ_i (Hz)
F	Faraday constant, $96487 C mol^{-1}$
I	electrolysis current (A)
J	electrolysis current density ($mA cm^{-2}$)
k	slope of the linear potential increase ($V s^{-1}$), see Fig. 1
n	number of electrons involved in the reaction to form one molecule of the dissolved gas
r_b	radius of a spherical glass ball (m)
r_e	radius of the disk electrode (m)
R_e	electrolyte resistance (Ω)
R_p	polarization resistance (Ω)
R_t	charge transfer resistance (Ω)
u_1	distribution function of the time intervals between two successive bubble departures (s^{-1})
v_g	mean volume of gas evolved per unit time ($m^3 s^{-1}$)
v_t	gas equivalent volume produced in molecular form per unit time ($m^3 s^{-1}$)
V_0	gas molar volume, $24.5 \times 10^{-3} m^3$ at 298 K
x_0	time pseudoperiod of bubbles evolution (s)
Z	electrode electrochemical impedance (Ω)

Greek characters

α_e	dimensionless proportional factor (Equation 19)
β	slope of $\log \lambda / \log J$ and $\log e / \log J$ curves
λ	number of bubbles evolved per unit time (s^{-1})
η_a	activation overpotential (V)
η_{ci}	concentration overpotential of reacting ionic species (V)
η_{cs}	concentration overpotential of dissolved molecular gas (V)
η_{ohm}	ohmic overpotential (V)
η_t	total overpotential (V)
ν	parameter characteristic of the gas evolution pseudoperiodicity, Equation 13 (s^{-1})
τ	time constant of the double layer capacity change (s)
ψ_v	power spectral density (psd) of the potential fluctuations ($V^2 Hz^{-1}$)
ψ_i	power spectral density (psd) of the current fluctuations ($A^2 Hz^{-1}$)

Special symbols

$\bar{\eta}_j$	spatial average of the overpotential η_j over the electrode surface
$\overline{\eta_{j,o}}$	time averaged value of $\bar{\eta}_j$
$\Delta \eta_j$	fluctuation of $\bar{\eta}_j$ around $\overline{\eta_{j,o}}$
$\langle \Delta \eta \rangle$	mean value of the total overpotential jump amplitude due to a bubble departure
$\langle \Delta I \rangle$	mean value of the current jump amplitude due to a bubble departure

1. Introduction

Electrolytically generated bubbles induce an increase of the electrode overpotential under current control. The literature is mainly concerned with the ohmic drop

increase [1-4]; only recently Leistra and Sides [5] and Dukovic and Tobias [6] detailed the three components of the overpotential increase: ohmic, kinetic and concentration effects.

The overpotentials given in the literature are time

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