Poison effects on hydrogen entry into palladium membranes using transfer function techniques

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Introduction

Hydrogen absorption into metals has been studied intensively by ac-impedance spectroscopy.[1-4] In the present work we have studied mechanism of poisons on hydrogen adsorption and absorption into palladium membranes. Baldauf and Kolb[5] showed, using cyclic voltammetry, that crystal violet blocks adsorption sites for hydrogen but influences favorably absorption reaction. Using permeation cells, the effect of crystal violet was studied using transfer function techniques in transmissive and reflective conditions in 0.1 M H_2SO_4.

Theory

The hydrogen evolution reaction (HER) in acidic solutions proceeds in two steps. The first one is the hydrogen adsorption (Volmer) on a metal M:

$$H^+ + M + e \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MH_{ads} \qquad (1)$$

It may be followed by electrochemical (Heyrovsky) or chemical (Tafel) desorption steps. Adsorbed hydrogen is also absorbed and diffuses into the metal:

$$MH_{ads} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} MH_{abs} \rightarrow \text{diffusion} \qquad (2)$$

Direct absorption model was also proposed[6,7]:

$$H^+ + M + e \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} MH_{abs} \rightarrow \text{diffusion} \qquad (3)$$

The total impedance of these reactions is given as

$$Z = R_S + \cfrac{1}{(j\omega)^{\phi} T + \cfrac{1}{Z_f}} \qquad (4)$$

where faradaic impedance Z_f is

$$Z_f = R_{ct} + \cfrac{1}{j\omega C_p + R_p^{-1} + \cfrac{1}{R_{ab} + Z_W}} \qquad (5)$$

R_{ct} is the charge transfer resistance, C_p pseudocapacitance, R_p the HER resistance, R_{ab} is the absorption resistance and Z_W is the Warburg impedance. The Warburg impedance Z_W in the case of transmissive conditions, where H is oxidized on the opposite side of the Pd membrane, taking into account constant phase behavior, may be described as:

$$Z_W = \frac{\sigma' l}{D_H \left(\sqrt{\frac{j\omega}{D_H}} l \right)^{\phi^W}} \tanh \left(\sqrt{\frac{j\omega}{D_H}} l \right)^{\phi^W} \qquad (6)$$

In reflective conditions, tanh in equation (6) is replaced by coth.

Results and discussion

Impedances and other transfer functions were determined in the Devenathan-Stachursky cell on Pd membranes in 0.1 M H_2SO_4 in the absence and presence of crystal violet and other poisons.

Fig. 1 shows an example of the transfer function $\Delta E_e/\Delta I_e$ determined at the entry side at the overpotential of 150 mV, on Pd membrane (50 μm) with the exit side kept at the potential of 525 mV. Addition of 10^{-4} M crystal violet caused increase of the charge transfer resistance corresponding to the H adsorption, reaction (1), and increase of the radius of the diffusional loop. Using CNLS fitting method, parameters of the total impedance were determined. Fig. 2 shows the dependence of R_{ct} on overpotential in the absence and presence of the poison.

Other poisons were also studied and kinetic-diffusion parameters were determined. The mechanism of poisoning and its influence on hydrogen absorption will be discussed.

References

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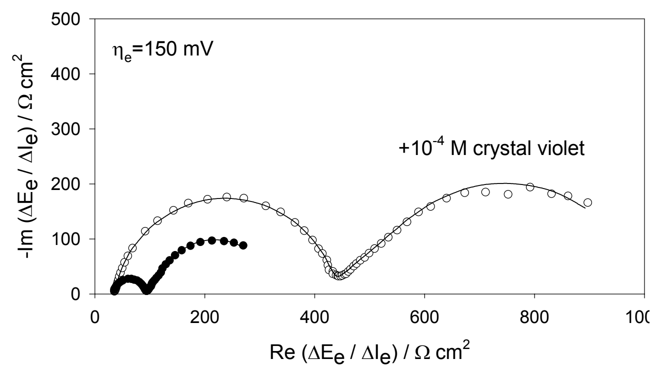

Fig. 1. Entry side transfer function $\Delta E_e/\Delta I_e$ in transmissive conditions at a 50 μm thick Pd membrane in 0.1 M H_2SO_4 before and after addition of 10^{-4} M crystal violet.

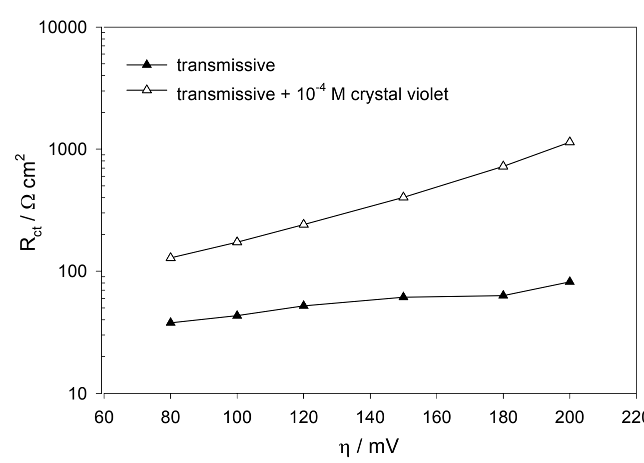

Fig. 2. Dependence of R_{ct} on entry overpotential in transmissive conditions on a 50 μm thick Pd membrane in 0.1 M H_2SO_4 before and after addition of 10^{-4} M crystal violet.