Determination of kinetic parameters in the Point Defect Model (PDM) for iron using electrochemical impedance spectroscopy (EIS) and DFT calculations

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Abstract In order to predict the general corrosion damage to metals and alloys, the acquisition of various kinetic parameters is of paramount significance. Electrochemical impedance spectroscopy (EIS) is a crucial technique for revealing the electrode kinetics. Equivalent circuit model composed of circuit components to analyze the values of components from EIS data, effectively distinguishes the “better or worse” corrosion resistance of different materials, but is short of dynamic information. Macdonald et al. developed a promising approach to optimize EIS data to acquire the kinetic parameters (such as transfer coefficients and rate constants, diffusion coefficients of defects) for passivated electrodes on the basis of the Point Defect Model (PDM). However, it is difficult to obtain the unequivocal values from optimization of EIS data because of too many unknowns. Herein, a theoretical method for independently estimating some parameters in the PDM from Mott-Schottky analysis is developed, such as polarizability α, β, and transfer coefficient of α_5, α_6. We reduce the number of unknowns in the optimization procedure, and thereby greatly improving the ability of the optimization procedure to determine accurate values for the remaining parameters in the PDM. For iron in borate buffer solution, the transfer coefficients of α_2, α_3, α_5, α_6 and α_7 are determined as 0.277, 0.003, 0.146, 0.219 and 0.961, and the rate constants of k_2^0、k_3^0、k_5^0、k_6^0和k_7^0为 6.626×10^{-12} mol/(cm^2 s), 6.492×10^{-6} mol/(cm^2 s), 6.075×10^{-8} mol/(cm^2 s), 5.512×10^{-7} mol/(cm^2 s) and 10^{-5}~10^{-3} mol/(cm^2 s), respectively. The electric field strength within passive film of iron is independent of the applied potential and pH of solution, with a value of 4.474 MV/cm. DFT calculations and experiment results validate the obtained rate constants from optimizing EIS data.

Keywords Passivity; Kinetic parameters; EIS; Point Defect Model

Reference

[1] D. Chen, J. Pan, F. Mao, G.R. Engelhardt, C. Dong, D.D. Macdonald, Linear dependence of potential drop at the passive film/solution interface on film-formation

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