

ELECTROCHEMICAL REDUCTION OF Fe(III) AT VARIOUS SURFACE STATES OF PLATINUM ELECTRODE

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Surface states of a platinum electrode are well understood today. These have been broadly classified as: (a) Active surface; (b) Oxidized surface; (c) Stripped surface; (d) Aged active surface; and (e) Aged oxidized surface.

In addition to these, James P. Hoare and coworkers (J. P. Hoare, 1963-1971) have studied passivated platinum surface and concluded that nitric acid treatment produces Pt-O alloy which is an electrode material having different catalytic and electronic properties from untreated platinum.

A voltammetric cell has been designed in which the pretreatment of the electrode surface is done out of the test solution in such a way that the electrode is neither exposed to the atmosphere nor comes in contact with any chemical other than the supporting electrolyte.

Fe(III) reduction has been studied on active and passivated electrode surfaces of (i) a rotating platinum wire electrode and (ii) a stationary platinum wire electrode by cyclic voltammetry. The results obtained using RPE are found to be greatly influenced by the initially applied potential and the time for which the electrode is held at the initial potential. On the basis of this, platinum surface states have been further classified as : $0.6A_{1/2}$, $0.7A_{1/2}$, $0.8A_{1/2}$, $0.9A_{1/2}$, $1.0A_{1/2}$, $0.6P_{1/2}$, $0.7P_{1/2}$, $0.8P_{1/2}$, $0.9P_{1/2}$, $1.0P_{1/2}$... $0.7P_5$ etc.

In the above classification, A stands for "active" surface whereas P stands for "passivated" surface. The prefix represents the initially applied potential and the suffix indicates the time in minutes for which the electrode is held at initially applied potential.

Study with rotating platinum wire electrode shows that Fe(III) reduction is reversible at $0.7P_{1/2}$ surface. The reversibility decreases as we move from $0.7P_{1/2}$ to $1.0P_{1/2}$ surface. When the reduction is studied on active surfaces it is most irreversible on $0.6A_{1/2}$ surface and the reversibility increases gradually from $0.6A_{1/2}$ to $1.0A_{1/2}$. The I-V curves at $1.0A$ surfaces are always associated with a prewave whereas a well defined single wave is observed on $1.0P$ surfaces. The I-V curves on passivated surfaces are generally found to be associated with a maximum.

Cyclic voltammetry reveals the reduction of Fe(III) on passivated surfaces to be a mixed phenomenon. The 10^3K_s as determined on $0.7A_{1/2}$, $0.8A_{1/2}$ and $0.9A_{1/2}$ surfaces comes out to be 3.9, 4.7 and 10.4 cm²/sec respectively. At $1.0A_{1/2}$ surface the peak separation is near to 60mV and hence evaluation of K_s is not possible.

The anodic peak potentials do not change as we move from $0.7A_{1/2}$ to $0.8A_{1/2}$ surface whereas cathodic peak potential increase for (i.e., becomes more anodic) this change. For $0.9A_{1/2}$ and $1.0A_{1/2}$ surfaces a slight change in the anodic

peak potentials is also observed. Anodic peak potential at sweep rate of 10mV/sec are same for $0.7A_{1/2}$, $0.8A_{1/2}$, $0.9A_{1/2}$ and $1.0A_{1/2}$ surfaces. For a given concentration of Fe(III) the peak currents observed are same for $0.7A_{1/2}$, $0.8A_{1/2}$, $0.9A_{1/2}$ and $1.0A_{1/2}$ surfaces. The peak currents are found to be directly proportional to the square root of sweep rate.

Keywords : Electrochemical Reduction; Fe(III); Surface States; Platinum Electrode

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Discussion

S. GURUSWAMY (*Central Electrochemical Research Institute, Karaikudi*): There are 4 states of isotopes of Fe, 54, 56, 57 & 58. Will it not be necessary to take this modern knowledge in our interpretations in electrochemistry ?

R. C. KAPOOR (*Department of Chemistry, University of Jodhpur, Jodhpur*): I doubt if such differences can be discerned by our technique.

B. M. GRAFOV (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*): 1. I cannot catch what is theoretical basis for calculating of rate constant k_s from voltammetricgram ? 2. Must you assume that rate constant k_s does not change during the cycle of voltammetricgram ?

R. C. KAPOOR : 1. At high sweep rate the kinetics of electrode transfer becomes competitive with the rate of potential change. Under these conditions the separation of the peak potentials would be a measure of standard rate constant. A theoretical correlation between peak potentials, standard rate constant and sweep rate has been worked out and applied successfully by Nicholson. 2. The rate constant changes during the cyclic voltammogram. The rate constants calculable on the basis of equations is the standard rate constant at $E = F^\circ$.