Calculations of the exchange current density for hydrogen electrode reactions: A short review and a new equation

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ABSTRACT

After reviewing relevant equations for the calculation of exchange current density, a new equation is derived for hydrogen electrode reactions to correct for the influences of the hydrogen concentration change in the vicinity to the electrode surface. This equation is able to describe the polarization curve shape in the small polarization region as well as to calculate the exchange current (density). The abilities of this equation are demonstrated by the data obtained with a Pt rotating disk electrode in 0.1 mol l^{-1} KOH solution. The exchange current density at 298 K under 1 atmosphere hydrogen pressure is found to be 0.103 mA cm^{-2} with an apparent activation energy of 33.5 kJ mol^{-1}. At a constant temperature, the exchange current is found to be proportional to the square root of the hydrogen partial pressure in the solution.

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1. Introduction

The hydrogen electrode reactions, including hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER), are among the most important reactions in electrochemistry and the exchange current (density), i_0, has been widely used as a parameter to evaluate the relevant catalysts in technical applications, such as fuel cells and water electrolyses. As well-known, the solubility of dihydrogen in aqueous solutions is rather low and this makes experimental determination of i_0 difficult for catalysts highly active to the hydrogen reactions.

In order to obtain i_0 as a characteristic for a given electrochemical system, either the Tafel plot in large overpotential region or the linear equation in small overpotential region may be used, in principle. However, for hydrogen reaction catalysts, it is better to deduce i_0 from low overpotential measurements. This is because the catalyst surface may change with potential and the parameter extrapolated from the large overpotential region may not reflect the real situation round the reversible hydrogen electrode potential (RHE). On the other hand, the real overpotential of a technical hydrogen electrode is usually not high (no more than one-tenth of a volt), the i_0 obtained from measurements round the RHE is certainly more applicable than those obtained by extrapolating from large overpotential measurements. Therefore, we shall concentrate on the equations for small overpotential in this paper.

Pt has been the best catalyst for the hydrogen reactions. In the early stage of electrochemistry, the reported i_0 values for the hydrogen reactions at Pt electrodes were obtained without the correction for the concentration polarization [1–12]. Since 1970s, it has been realized that the concentration overpotential is not negligible even at low overpotentials for Pt. For catalysts other than Pt, the same problem appears as long as the catalytic activity becomes high. Therefore, it is necessary to work out an equation which is able to correct properly for the influences of the hydrogen concentration changes in the vicinity of the electrode surface. There have been a few such equations found in the literature, but they were somewhat different from each other. In this paper, we shall first review these equations and compare them in two aspects, i.e., the deduction of i_0 and the description of the polarization curve shape in low overpotential region; and then we shall derivate a new equation, which is of higher accuracy in polarization curve description and yet simple in form, and verify it using experimental data obtained with a Pt rotating disk electrode (RDE) in KOH solutions.

The reason for choosing KOH solution, rather than H$_2$SO$_4$ solution, in the present work was that the hydrogen electrode reactions in alkaline media are kinetically slower than in acidic media, so that we can readily verify the ability of the equations for i_0 calculation. For a Pt RDE in acidic solutions, the exchange current is too large to be determined by conventionally RDE method but is accessible for carbon-diluted Pt/C using the equations derived in this paper [13].

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2. Experimental

The data of hydrogen reactions at Pt electrodes in alkaline solutions were obtained by carrying out electrochemical measurements with a single compartment cell which was equipped with a water jacket for temperature control. The working electrode was a Pt RDE (Autolab, Mode ECO CHEMIE BV), and the counter electrode was a Pt wire. The reference electrode was an RHE [14] in the same solution as that in the cell and was connected to the cell through a Luggin capillary. All solutions were prepared using carefully purified water, which was obtained by distillation of the 18 MΩ cm deionized water with $KMnO_4$ to remove traces of organics. Measurements were conducted on an electrochemical analyzer (CHI 634, Shanghai).

Before electrochemical measurements, the Pt electrode was polished with alumina powers successively from 0.3 to 0.05 μm and then carefully washed with acetone and deionized water. The polished Pt electrode was pretreated and characterized by cyclic voltammetry (CV) in 0.5 mol l^{-1} H_2SO_4 purged with high purity N_2 gas (99.999%) till the standard CV was obtained. Then the Pt electrode was washed with water thoroughly and transferred into the cell containing 0.1 mol l^{-1} KOH solution that was saturated by high purity hydrogen. The electrode was conditioned again by CV over 0.05–1.3 V (versus RHE), till reproducible CV curves were obtained.

Immediately after surface conditioning, a slow potential scan was performed from −0.05 to 0.45 V to obtained a steady state polarization curve. Fig. 1 shows a set of typical polarization curves acquired at different rotation rates. On the cathodic branch (negative to RHE), the hydrogen evolution current increases quickly with potential moving to the negative. On the anodic branch (positive to RHE), with the increase of potential, the hydrogen oxidation current increases first and then levels off. A careful inspection into Fig. 1 would find that the plateaus are not really flat. When the pseudo-plateau currents taken at 0.3 V were plotted against the square root of rotating rates, a slightly curved line resulted as shown by the solid line in Fig. 2. It can be seen that the pseudo-plateau currents deviated from the expected proportionality (the dashed line in Fig. 2) for high rotating rates, indicating an influence of kinetic limitation. The kinetic limitation would be seen more clearly at higher rotating rates. For example, at 6400 rpm, pseudo-plateau current was found to be about 20% than the extrapolated (not shown in Fig. 2). In order to reduce the influence of the kinetic limitation, we concentrated on relatively low rotating rates and made corrections by extrapolating from the initial slope as shown in Fig. 2 where the corrected mass-transport limiting currents are marked by the numbers close to the open diamonds.
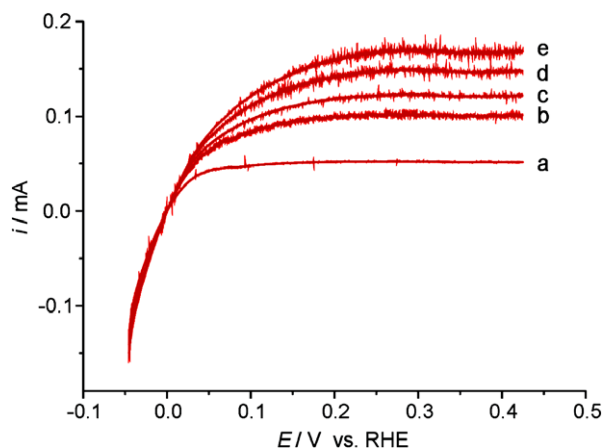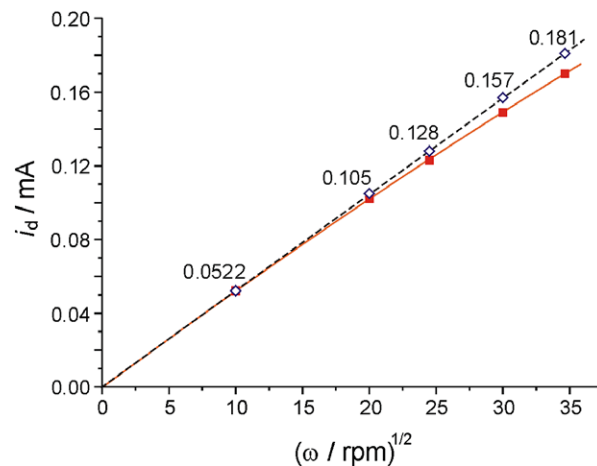

Fig. 2. Pseudo-plateau currents (filled squares) and extrapolated mass-transport limiting currents (open diamonds) for different rotation rates.

Fig. 3 shows the plot of normalized current, $i/i_{a,d}$, versus polarization in the small overpotential region; the deviation of the polarization curves from straight lines indicates the effects of concentration polarization.

3. Review of literature equations

In this section, we shall first present the general equations correcting for the influences of surface concentration changes, followed by a few literature equations specifically for the hydrogen reactions. In all the equations below, the anodic current (i_a) is defined as positive current; and the difference between the working potential (E) and the equilibrium potential (E_{eq}) as the overpotential (η), i.e., $\eta = E - E_{eq}$. According to these definitions, hydrogen oxidation and hydrogen evolution are accompanied by positive and negative overpotentials, respectively.

3.1. General equations

3.1.1. Concentration polarization correction for single-step one-electron reactions [15]

"Concentration polarization" is usually referred to the overpotential caused by the change of the concentrations in the vicinity of the electrode surface (surface concentration changes). In fact, the surface concentration change causes not only concentration
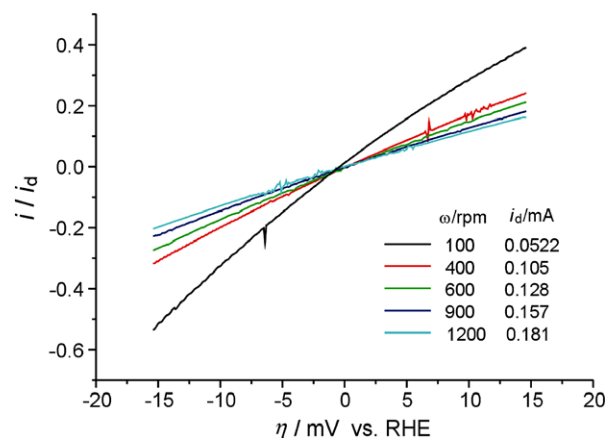

Fig. 1. Typical polarization curves of Pt RDE in hydrogen saturated 0.1 mol l^{-1} KOH solution (100, 400, 600, 900, and 1200 rpm for curves from a to e, respectively, 298 K).

Fig. 3. Plots of normalized currents versus overpotential (data originated from Figs. 2 and 3).