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A new method to analyze polarization curves — its application for the determination of kinetic parameters for oxygen reduction

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Abstract

A new method has been developed to analyze current–potential curves. The treatment was applied to determine the kinetic parameters of oxygen reduction. The reduction of oxygen was studied on thin-film platinum electrodes in alkaline solution. For the purpose of comparison the kinetic parameters were determined by the traditional method of constructing Tafel plots.

Keywords: Kinetic parameters; Electrode kinetics; Oxygen reduction; Platinum; Voltammetry

1. Introduction

The oxygen reduction reaction has been widely studied because of the application of oxygen cathodes in electrochemical energy conversion systems [1–3]. Platinum is one of the best catalysts for oxygen reduction. However, the mechanism of oxygen reduction on platinum is still open for debate [1,2]. It has been generally recognized that the rate-determining step of oxygen reduction on the Pt electrode involves the transfer of the first electron to the oxygen molecule. This is accompanied by the adsorption step of oxygen on the electrode surface [4]. There has been a consensus on the fact that the slope of the Tafel lines determined in the region of low current densities is close to -60 mV dec^{-1}. The experimental slope value differs from the predicted one (-120 mV dec^{-1}) due to the effect of the adsorbed oxygen-containing species [5,6]. There has been extensive experimental evidence that the Tafel slope increases at more negative potentials in alkaline solution [6–10]. This has been attributed to the chemical rate-determining step. Recently, the reduction of oxygen has been studied on thin-film Pt electrodes in alkaline solution [11,12]. Even 1 nm thick Pt films showed remarkable activity in the oxygen reduction reaction. Platinum thin films on flat substrates can be used as a model system for highly dispersed platinum on carbon support [12].

Usually, the kinetic parameters of electrochemical reactions have been determined from Tafel plots [13]. In a recent publication, Frumin and Zilberstein [14] proposed a new approach to treat the current–voltage data. They used a sophisticated statistical method to determine the kinetic parameters of electrode reactions.

In this communication we report a new method to analyze the polarization curves of slow reactions. The reduction of oxygen was studied and the voltammetric data were analyzed by applying the proposed procedure. For comparative purposes the conventional method of constructing Tafel plots was used to obtain the kinetic parameters of oxygen reduction.

2. Theoretical model

Our main idea is to analyze the current–potential curves in a differential form. This approach makes it possible to obtain kinetic parameters without the need to construct Tafel plots. Differentiation of the kinetic expression of an irreversible cathodic reaction (Eq. (1)) yields Eq. (2):

$$i = nFACk^{o} \exp\left[-\frac{\alpha z F (E - E^{o'})}{RT} \right] \quad (1)$$

where n is the number of electrons accepted, F the Faraday constant, A the electrode area, C the concentration of the reactant, k^o the standard heterogeneous rate constant, α the transfer coefficient, z the number of electrons involved in the

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rate-determining step and $E^{o'}$ the formal potential of an electrode. The term $-2.303RT/azF$ is the Tafel slope b.

$$\frac{di}{dE} = nFACk^{o}\left(-\frac{\alpha zF}{RT}\right)\exp\left[-\frac{\alpha zF(E-E^{o'})}{RT}\right] \quad (2)$$

where di/dE is the slope of the polarization curve at a given potential. In order that this treatment might be correct, n must be constant in the potential range studied. Combining Eqs. (1) and (2) gives

$$\frac{di}{dE} = -\frac{i\alpha zF}{RT} = \frac{2.3i}{b} \quad (3)$$

For the process under combined kinetic and mass-transfer control the cathodic current can be expressed by

$$i = \frac{nFAC}{1/k_d + (1/k^{o})\exp[\alpha zF(E-E^{o'})/RT]} \quad (4)$$

where k_d is the diffusion rate constant [13]. In Eq. (4), $k_d = D/\delta$ where D is the diffusion coefficient and δ the diffusion layer thickness. Eq. (4) can be simplified by substituting i_d for $nFAk_dC$, where i_d is the diffusion-limited current:

$$i = \frac{i_d}{1 + (k_d/k^{o})\exp[\alpha zF(E-E^{o'})/RT]} \quad (5)$$

Rearranging Eq. (5) yields

$$\frac{k_d}{k^{o}}\exp\left[\frac{\alpha zF(E-E^{o'})}{RT}\right] = \frac{i_d - i}{i} \quad (6)$$

Differentiation of Eq. (6) yields the following expression:

$$\frac{di}{dE} = -\frac{i^2}{i_d}\frac{\alpha zF}{RT}\frac{k_d}{k^{o}}\exp\left[\frac{\alpha zF(E-E^{o'})}{RT}\right] \quad (7)$$

Combining Eqs. (6) and (7) to eliminate $(k_d/k^{o})\exp[\alpha zF(E-E^{o'})/RT]$ gives

$$\frac{di}{dE} = -\frac{i\alpha zF}{RT}\left(1-\frac{i}{i_d}\right) = \frac{2.3i}{b}\left(1-\frac{i}{i_d}\right) \quad (8)$$

This equation allows the calculation of the Tafel slope values from the experimental current–potential data from which the background current has been subtracted. Modern electrochemical equipment and computer software enable us to perform these calculations fairly easily.

$$b = 2.3i\frac{dE}{di}\left(1-\frac{i}{i_d}\right) \quad (9)$$

Finally, we can calculate the kinetic parameters of interest (i_o, k^{o}) for the cathodic process under study:

$$i_o = \frac{1}{A}\exp\left[\frac{\alpha zF(E-E_r)}{RT}\right]\frac{ii_d}{i_d - i} \quad (10)$$

where E_r is the equilibrium potential of an electrode:

$$k^{o} = \frac{1}{nFAC}\exp\left[\frac{\alpha zF(E-E^{o'})}{RT}\right]\frac{ii_d}{i_d - i} \quad (11)$$

When deriving these expressions we assumed that the electrode was flat. Working with solid electrodes one should make a correction for a roughness factor (f_r). Therefore, the surface area (A) in Eqs. (10) and (11) should be multiplied by f_r.

3. Experimental

Thin platinum films (10 nm thick) were prepared by vacuum evaporation at a base pressure of 2×10^{-6} Torr. Glassy carbon (GC) was used as a substrate material. The GC disk with an exposed area of 0.125 cm^2 was inserted into a Teflon sheath. The front surface of the GC disks was polished to a mirror finish with a 0.3 μm alumina slurry in distilled water. After alumina polishing the electrodes were sonicated twice for 3 min.

Electrochemical measurements were performed in 0.1 M KOH solution by employing the rotating disk electrode (RDE) technique. The solution was prepared from KOH pellets (p.a. quality, Merck) and Milli-Q water (Millipore, Inc.). The solution was saturated with pure oxygen (99.95%, AGA). An EDI 101 rotating disk electrode and a CTV speed control unit (Radiometer) were used for the RDE experiments. The following rotation rates were applied: 360, 610, 960, 1800, 3100 and 4600 rpm. A saturated calomel electrode (SCE) was used as a reference, and a Pt foil served as a counter electrode. An Autolab potentiostat/galvanostat PGSTAT10 (Eco Chemie B.V.) was used to polarize the electrodes. The potentiostat was controlled by the General Purpose Electrochemical System (GPES) software.

4. Results and discussion

Before starting the oxygen reduction experiments the thin-film Pt electrodes were cycled in the potential range from 0.4 to −0.9 V (SCE) in Ar-saturated 0.1 M KOH solution in order to activate the electrodes. This treatment makes it possible to obtain data that are more reproducible. Voltammetric measurements of oxygen reduction were performed with slightly preoxidized thin-film Pt electrodes by holding the electrode at 0.12 V for 1 min before each polarization measurement. The RDE voltammetry curves for oxygen reduction on a 10 nm thick Pt film are presented in Fig. 1. The Koutecky–Levich analysis revealed that the number of electrons transferred per oxygen molecule is close to four (the inverse slope of the K–L plot was 0.434 ± 0.005 mA cm^{-2} $rad^{-1/2}$ $s^{1/2}$). Mass-transfer corrected Tafel plots were constructed to determine the kinetic parameters of oxygen reduction (Fig. 2). This is the most frequently employed method to analyze the RDE data. As is typical for a platinum electrode the slope of the Tafel lines was close to −60 mV dec^{-1} in the low current density region. The slope was independent of the

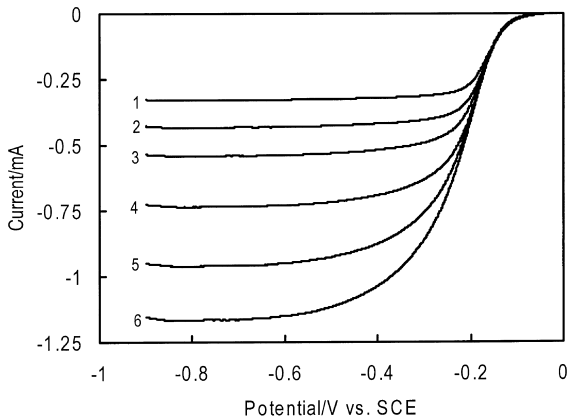

Fig. 1. Voltammetry curves for oxygen reduction on a thin-film Pt electrode in oxygen-saturated 0.1 M KOH. Rotation rate: (1) 360; (2) 610; (3) 960; (4) 1800; (5) 3100 and (6) 4600 rpm. Sweep rate 10 mV s^{-1}.

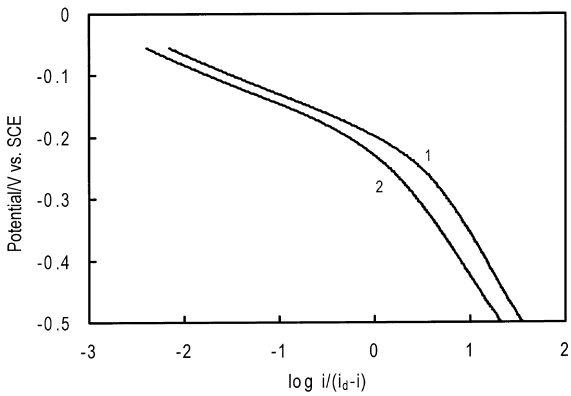

Fig. 2. Mass-transport corrected Tafel plots for oxygen reduction on a thin-film Pt electrode. Data derived from Fig. 1. Rotation rate: (1) 1800 and (2) 4600 rpm.

electrode rotation rate. The first Tafel region of the constant slope extended about 130 mV. This was followed by a short region in which the Tafel slope gradually changed. A rapid change in the surface coverage by adsorbed oxygen-containing species started in the same potential region. It was stated that the change of the slope occurs at potentials at which the coverage by adsorbed oxygen is below the critical level [5,6]. The slope of the Tafel lines increased at high overpotentials. The high slope value indicates a change in the mechanism of oxygen reduction. A slope value close to -260 mV dec^{-1} was obtained for a 10 nm thick Pt electrode in the second Tafel region. In accordance with our previous study [11] the exchange current density of oxygen reduction was 3.2×10^{-10} A cm^{-2}. Kinetic data were obtained from the cathodic potential scan, thus corresponding to the initially oxidized electrode surface.

It is of special interest to compare the kinetic parameters obtained from the Tafel plots with those calculated by the new methodology. Fig. 3 presents the dependence of the Tafel slope on electrode potential. The slope values were obtained by applying the treatment presented in Section 2. It is relevant to note that, owing to the differentiation of the *i–E* curves, the experimental data must be of good quality in order to

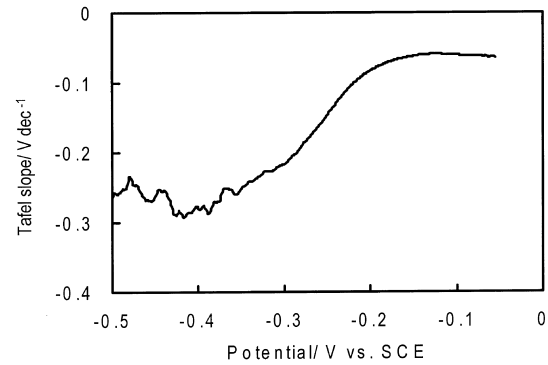

Fig. 3. Dependence of the Tafel slope on potential. The slope values were calculated by Eq. (9). $\omega=1800$ rpm.

obtain reliable Tafel slope values, otherwise the scattering of data will be too large. In fact it is rather complicated to determine the slope values at the very beginning of the polarization curve because of the difficulties in the correction for the background level. Analogously, the differentiation of the data seems to be a considerable problem at the potentials close to the region of diffusion control. Moreover, the $(1-i/i_d)$ component needs to be precisely determined at high current densities due to the proximity of the measured current to the limiting one. It is advisable to select the data in a suitable current window for further analysis. As usual, the smoothed data allow us to make a more accurate kinetic analysis. The average Tafel slope value calculated by Eq. (9) at low overpotentials was -61 mV dec^{-1}.

For comparison, the exchange current densities were also calculated by Eq. (10) using the Tafel slope values computed by Eq. (9). In this case one can obtain the i_o value at every experimental point over the entire polarization curve. However, from the practical point of view the i_o values obtained at low overpotentials are of greatest interest. An average exchange current density, determined in the first Tafel region, was 4.3×10^{-10} A cm^{-2}. As expected, this value coincided perfectly with the i_o value determined by the conventional method.

The advantage of the methodology given above is not only to treat the polarization curves in order to determine the kinetic parameters of electrochemical reactions, but also to enable the researchers to simulate the current–potential curves by applying certain values for parameters in Eq. (4). For example, Fig. 4 presents the kinetic (curve 1), simulated (curve 2) and experimental (curve 3) currents for oxygen reduction on a thin-film Pt electrode. When constructing the kinetic and simulated curves it was assumed that the Tafel slope of -61 mV dec^{-1} holds for the entire potential region. The apparent rate constant (k^o) used in Eq. (4) was determined from the RDE data (Fig. 1) in the low current density region where the Tafel slope is nearly constant (Fig. 3). It is clearly seen in Fig. 4 that at the foot of the polarization curve the process of oxygen reduction is totally under kinetic control. In the potential region from -0.125 to -0.175 V the measured current coincides with the theoretically calculated

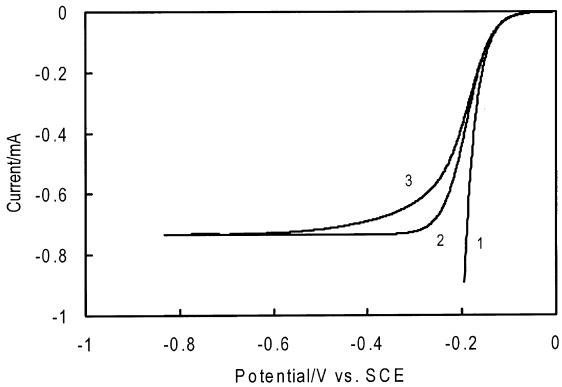

Fig. 4. Experimental (3) and simulated (2) current–potential curves for oxygen reduction on a thin-film Pt electrode in oxygen-saturated 0.1 M KOH at a rotation rate of 1800 rpm and a sweep rate of 10 mV s^{-1}. Curve (1) represents the dependence of kinetic current on potential.

one. At higher overpotentials the experimental curve deviates from the theoretical curve. This can be explained by a change in the rate-determining step, as mentioned above.

5. Conclusions

We conclude that the procedure outlined in this paper is mathematically simple and makes it possible to determine easily the kinetic parameters of various charge-transfer reactions.

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