SHORT COMMUNICATION

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A note on overpotential dependence of AC impedance data

Abstract Charge-transfer resistance $[R_{ct} = (d\eta/di)_{\eta=0}]$ and Tafel plots of current density (i) versus overpotential (η) data are generally known to yield values of the energy-transfer coefficient (α) and exchange current density (i_o) of an electrochemical reaction. In the present investigation, the resistance $(d\eta/di)_{\eta\neq0}$ that could be calculated by differentiating a wide range of $i - \eta$ curves was also shown to provide the values of α and i_o, by plotting $\ln(d\eta/di)_{\eta\neq0}$ against η. Since α and i_o could also be evaluated directly from the experimental DC polarization data, the procedure was not of significant importance. Nevertheless, it was considered important in evaluating α and i_o from AC impedance data, because the procedure was based on data analysis, which was much simpler than that reported in the literature. A cobalt electrode prepared from fine metal powder was used in 1 M KOH electrolyte and the hydrogen evolution reaction was studied by AC impedance at several potentials. The resistance values measured from the complex plane impedance diagram were plotted against the potential, and the values of α and i_o were evaluated.

Key words DC polarization · AC impedance · Energy-transfer coefficient · Exchange current density

Introduction

Current density (i) and overpotential (η) of a charge-transfer controlled electrode process $(O + ne^- \rightarrow R)$ follow the Butler-Volmer relationship [1]:

$$i = i_o(e^{-\alpha nf\eta} - e^{(1-\alpha)nf\eta}) \tag{1}$$

where i_o is the exchange current density, α is the energy-transfer coefficient, n is number of electrons and $f = F/RT$. For the purpose of evaluating the kinetic parameters, viz., i_o and α, of the reaction, generally the $i - \eta$ data are used in two ways. If $|\eta| \ll 1/nf$, a plot of η versus i is linear (ohmic relationship) in the vicinity of $\eta = 0$, and the slope of the plot $(d\eta/di)_{\eta=0}$, which is known as charge-transfer resistance (R_{ct}), provides the value of i_o:

$$i_o = 1/nf(d\eta/di)_{\eta=0} \tag{2}$$

Alternately, if $|\eta| \gg 1/nf$, a plot of η versus $\ln i$ is linear. The value of i_o is obtained by extending the linear Tafel region of the plot to $\eta = 0$, and the value of α is obtained from the slope. The essential difference between the ohmic current-potential relationship and the exponential relationship is reflected in the η versus $\ln i$ plots. Another way of distinguishing these two types of relationships is the resistance $(= d\eta/di)$ at $\eta \neq 0$, which is not generally referred to in the literature. The value of $(d\eta/di)_{\eta\neq0}$ is a constant with a variation of η or i in the case of the ohmic type of relationship. On the other hand, it varies with a variation of η or i in the case of the exponential relationship. In the present investigations, it is shown that $(d\eta/di)_{\eta\neq0}$ of $i - \eta$ data can also be used to evaluate the values of α and i_o. By extending the above procedure to AC impedance data, the values of the electrochemical resistance of the hydrogen evolution reaction measured at several potential values are shown to yield the values of i_o and α.

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Experimental

Thin pellet-type electrodes of 0.2 cm^2 geometric area were made by compacting fine particles (average size $\approx$20 nm) of cobalt powder, which was synthesized by a polyol method. A nickel wire served as the current collector. A solution of 1 M KOH was prepared in doubly distilled water and pre-electrolyzed before use. The elec-

trochemical cell contained a cobalt electrode, which was placed symmetrically between two large-size (3.8×3.5 cm) nickel sheet counter electrodes and a Hg/HgO, 1 M KOH reference electrode. The working electrode was cathodically polarized at a current density of 0.5 A cm^{-2} for about 5 h and allowed to reach equilibrium for several hours after cessation of current. During open-circuit conditions, the electrolyte was purged with hydrogen gas. AC impedance of the cell was measured in the frequency range from 100 kHz to 10 mHz at an excitation signal of 5 mV by using an Electrochemical Impedance Analyzer (EG&G PARC model 6310) which was driven by an IBM compatible computer. The resistance values contained in the impedance data were evaluated by a NLLS fitting program of Boukamp and supplied by EG&G PARC [2], similar to an earlier report [3]. As the area of the counter electrode was larger than the working electrode area by about 130 times, the measured impedance of the cell was attributed to the impedance of the working electrode alone.

Results and discussion

For a single electron-transfer reaction, such as a hydrogen evolution reaction in an alkaline electrolyte

$$H_2O + e^- \rightarrow \tfrac{1}{2} H_2 + OH^- \tag{3}$$

at overpotentials $-\eta \gg 1/f$, Eq. 1 may be reduced to Eq. 4:

$$i = i_o e^{-\alpha f \eta} \tag{4}$$

The above equation may be re-written as

$$\eta = (\ln i_o - \ln i)/\alpha f \tag{5}$$

By differentiation with respect to i, Eq. 6 is obtained:

$$(d\eta/di)_{\eta \neq 0} = -1/i\alpha f \tag{6}$$

Equation 6 suggests that the value of the resistance $(d\eta/di)_{\eta \neq 0}$ increases with i^{-1}. In the case of an ohmic type of relationship, the value of $(d\eta/di)_{\eta \neq 0}$ is expected to be invariant with η (or i), and corresponds to the resistance value of the ohmic component. Equation 6 may be further analyzed by substituting i with η from Eq. 4:

$$(d\eta/di)_{\eta \neq 0} = -e^{\alpha \eta f}/\alpha f i_o \tag{7}$$

or

$$\ln(-d\eta/di)_{\eta \neq 0} + \ln(\alpha f i_o) = \alpha \eta f \tag{8}$$

A plot of $\ln(-d\eta/di)_{\eta \neq 0}$ against η results in a straight line with a slope of (αf) and intercept of $\ln(\alpha f i_o)^{-1}$. Thus, it is possible to evaluate the values of both α and i_o. This procedure, however, is not of significant importance in evaluating the kinetic parameters from DC polarization data, since they can be evaluated more directly by plotting $\ln i$ versus η. Nevertheless, it may be employed to evaluate the kinetic parameters from AC impedance measurements.

Timmer et al. [4] derived theoretical expressions of the faradaic impedance as a function of potential. They assumed mass transfer due to the AC current and due to the DC current did not influence each other, and derived expressions involving complex functions. By plotting a function $\log \theta$ against potential, it was shown that the slope of the linear plot yielded the value of the energy-transfer coefficient and the intercept gave the value of the standard rate constant. The parameter $(d\eta/di)_{\eta \neq 0}$ in Eq. 8 is equal to the faradaic impedance, which can be obtained from the diameter of the semicircle of the Nyquist impedance plot. Equation 8 is much simpler than the expression given previously [4] and it is derived without involving any assumptions. Evaluation of α and i_o from AC impedance measurements using Eq. 8 is described below.

The hydrogen evolution reaction at a cobalt electrode in 1 M KOH was studied by AC impedance. The complex plane diagram of the impedance contained two semicircles as shown in Fig. 1a for the open circuit potential, E_{oc} ($= -0.830$ V vs. Hg/HgO, 1 M KOH), and in Fig. 1b for E ($= -1.045$ V vs. Hg/HgO, 1 M KOH). Similar types of impedance plots containing two semicircles have been reported in literature [5]. The low-frequency semicircle was attributed to a parallel combination of charge-transfer resistance of Eq. 3 and double-layer capacitance, whereas the high-frequency semicircle was not explained [5]. Several possibilities could be considered for the occurrence of an additional semicircle:

1. The electrode was made by compacting fine particles of cobalt metal. This might result in a resistance due to particle-to-particle contact and a capacitance associated with separation of charges in the electrode owing to compaction of particles. The presence of these elements in a parallel combination might result in the form of semicircle.

2. As the electrode constituted fine particles, surface oxidation of the particles could have resulted owing to the high reactive nature of the fine metal powder before the electrode was made. Although cobalt oxide was not present at a high concentration for detection by X-ray diffraction and the electrode was cathodically polarized under vigorous hydrogen evolution for a long time, it was possible that a small amount of cobalt oxide or cobalt hydroxide was present on the electrode. The additional semicircle could be attributed to the resistance and the capacitance of such surface cobalt compounds.

3. It is known that the mechanism of the hydrogen evolution reaction involves three steps (viz., Volmer, Herovsky and Tafel), of which the first two are electron-transfer steps. The charge-transfer resistance of the two steps might have reflected in two semicircles on the complex plane impedance diagram.

4. In the present studies, the measured open-circuit potential of the cobalt electrode was -0.830 V (vs. Hg/HgO, 1 M KOH), whereas the theoretical value of the reversible potential (E^r) was -0.926 V (vs. Hg/HgO, 1 M KOH) for Eq. 3. The open-circuit potential, therefore, was a mixed potential corresponding to a corrosion process. The pair of semicircles might be considered to correspond to the pair of partial
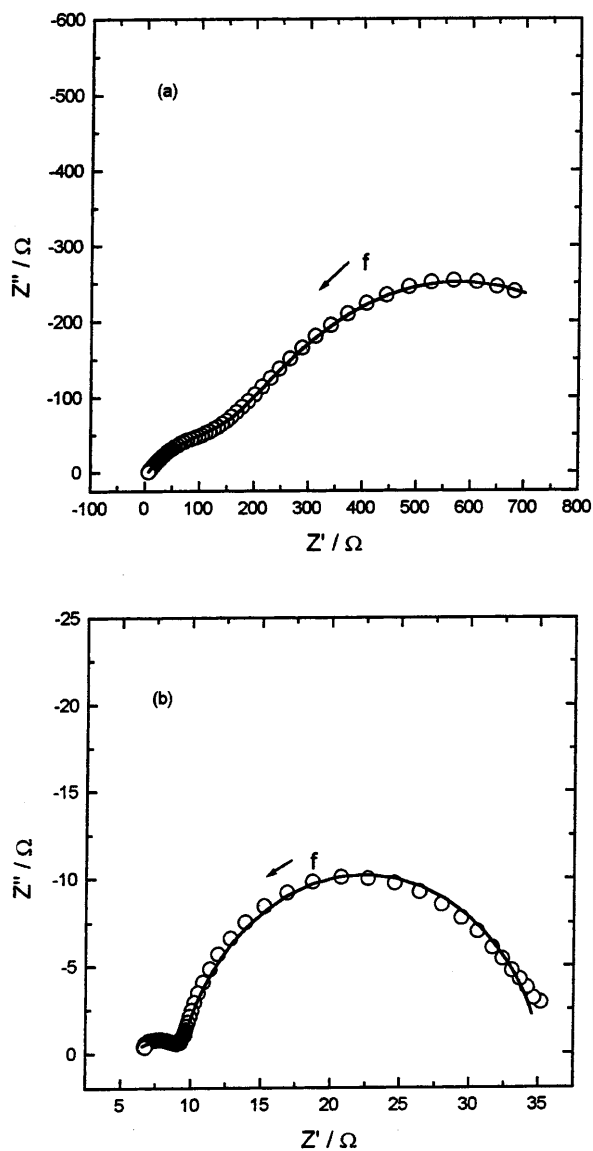
additional semicircle, which is discussed in the next paragraphs. The value of the resistance obtained from a semicircle of open-circuit impedance is generally considered equal to the charge-transfer resistance (R_{ct}) of the reaction, and i_o (or corrosion current density) is evaluated using Eq. 2 [6]. Comparative investigations of several fine metal particle electrodes, and kinetics and mechanism of hydrogen evolution reaction on them, are in progress in our laboratory.

AC impedance of the cobalt electrode was measured at several DC bias potentials under which the hydrogen evolution reaction occurred. At all potentials, the presence of two semicircles on the complex plane diagrams was consistent. Furthermore, there was a decrease in the size of both the semicircles with increase of overpotential, unlike in [5] where the high-frequency semicircle was reported invariant at a Ni-Al electrode. The data measured at E ($= -1.045$ V vs. Hg/HgO, 1 M KOH), for example, are shown in Fig. 1b. A decrease in the size in

Fig. 1 Complex plane plots of AC impedance of a cobalt electrode (0.2 cm^2) in 1 M KOH measured at open circuit potential ($E_{oc} = -0.830$ V vs. Hg/HgO, 1 M KOH) (**a**) and at $E = -1.045$ V (vs. Hg/HgO, 1 M KOH) (**b**) at 20 ± 1 °C. For the purpose of clarity the axes are not shown in equal scales. The experimental data points are shown as *open circles* and the curve-fit results are shown as a *solid line*

reactions of the corrosion process. This argument, however, did not explain the presence of two semicircles obtained at potentials more negative to -0.926 V (vs. Hg/HgO, 1 M KOH) where only hydrogen evolution reaction was possible.

Although it is not clear at the present time which of these is the most appropriate process responsible for an additional semicircle (Fig. 1), it was found that a pair of semicircles was reproduced with several electrodes made out of fine cobalt powder, electrodes containing cobalt and palladium powders as well as in concentrated KOH electrolytes. The possibility (1) above is ohmic in nature and is not an important factor for the appearance of an
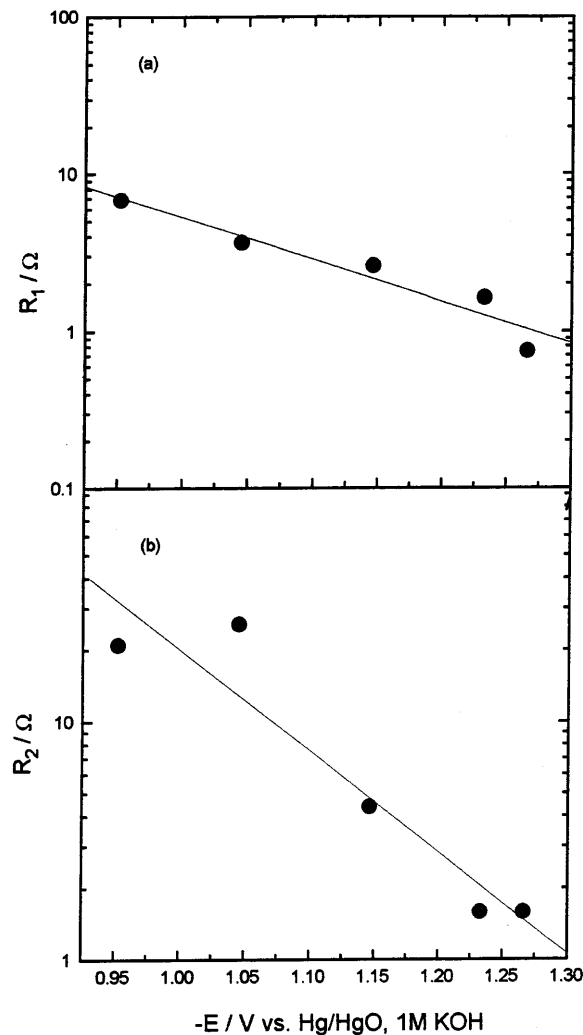

Fig. 2 Resistance (R_1) of the high-frequency semicircle and resistance (R_2) of the low-frequency semicircle as a function of the potential ($-E$) of a cobalt electrode (0.2 cm^2) in 1 M KOH at 20 ± 1 °C

the data of Fig. 1b may be noted in relation to the size of the data in Fig. 1a obtained at E_{oc} ($= -0.830$ V vs. Hg/HgO, 1 M KOH). A decrease in the sizes of both the semicircles with an increase of overpotential suggests that the related processes are electrochemical in nature. A pure ohmic circuit is not expected to vary in its values measured by AC impedance when biased by a DC voltage.

As the resistance (R) obtained from AC impedance at any DC potential is the same as the parameter $(d\eta/di)_{\eta \neq 0}$ of the $i - \eta$ data, R was analyzed using Eq. 8 to obtain the values of α and i_o of the corresponding electrochemical process. The values of the resistances obtained from the high-frequency semicircle (R_1) and low-frequency semicircle (R_2) at $E \geq -0.95$ V (vs. Hg/HgO, 1 M KOH) are plotted against $-E$ and are shown in Fig. 2. It was evident that R_1 and R_2 decreased linearly with an increase in $-E$, but for some experimental scatter. By an average linear fit of the data, values of the slopes of 2.66 ± 0.44 V^{-1} and 4.26 ± 0.82 V^{-1} and values of the intercepts of 8 Ω and 40 Ω at E^r ($= -0.926$ V vs. Hg/HgO, 1 M KOH) were obtained from Fig. 2a and b, respectively. The values of α calculated (Fig. 2 and Eq. 8) were 0.158 ± 0.025 and 0.255 ± 0.049 and those for i_o obtained were $(10.48 \pm 1.75) \times 10^{-2}$ A cm^{-2} and $(1.322 \pm 0.25) \times 10^{-3}$ A cm^{-2} for the processes corresponding to high-frequency and low-frequency semicircles, respectively.

Conclusions

The Butler-Volmer equation relating current density and overpotential of an electrochemical process has been extensively used in the literature. It was shown in the present studies that the derivative of $i - \eta$ plots, viz.

$(d\eta/di)_{\eta \neq 0}$, linearly increased with i^{-1}. The value of α and i_o were evaluated from $\ln(d\eta/di)_{\eta \neq 0}$ versus η plots. The decrease of resistance of the hydrogen evolution reaction obtained from AC impedance measurements with an increase of overpotential was explained based on $\ln(d\eta/di)_{\eta \neq 0}$ versus η behaviour, and the values of α and i_o were evaluated.

The AC impedance technique is employed for a variety of investigations in the current literature. It is possible that ohmic types of resistance constitute the measured impedance data. Grain boundary resistance of solid state conductors, contact resistance between particles of a conductor and an insulator of a composite material, etc., are typical examples of such ohmic resistance. It is shown in the present investigations that an ohmic type of resistance can be easily identified by noting non-variance of its value with the DC bias voltage.

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