CALORIMETRY OF ELECTRODE REACTION UNDER LINEAR SWEEP-CURRENT POLARIZATION

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Abstract

The mathematical–physical equation concerning the process of calorimetry of electrode reactions was deduced, and the corresponding solutions were obtained respectively for the period of the electrochemical polarization and that of the natural cooling. The calorimetry of the anodic oxidation of ferrocyanide to ferricyanide under linear sweep–current polarization was carried out, the obtained apparent enthalpy change of the electrode reaction agreed well with that obtained by the calorimetry with constant currents. The developed calorimetry with linear sweep–current and the data processing method are applicable for quick determination of apparent enthalpy changes of electrode reactions.

Keywords: electrode reaction, enthalpy change, sweep–current, thermoelectrochemistry

Introduction

The previous research on the calorimetry of electrode reactions were carried out mainly under constant current polarization [1–4], though cyclic–voltammo–thermometry involving very complicated mathematical deconvolution was put forward [5]. With the constant–current method, calorimetry have been done under a series of constant currents in order to obtain the thermoelectrochemical quantities such as the Peltier heat effect [2] and the apparent enthalpy change [4] of electrode reactions. In the present work, attempts were made to figure out the apparent enthalpy change of an electrode reaction from only one run of calorimetry carried out under linear sweep-current polarization, based on the derived mathematical–physical equation for the measurement.

Mathematical–physical equation

In this work, the electrode system was placed in a Calvet heat-conducting microcalorimeter, so that the heat generated by the electrode reaction and the electrical quantities can be measured simultaneously. In accordance with Tian Eq. [6], the heat flow rate produced by the reaction in a calorimeter is

$$H = A\left(E + K\,\frac{dE}{dt}\right) \qquad (1)$$

where H denotes the heat flow rate, E the electrical signal output by the calorimeter, t the time, A the static constant which can be calibrated with Joule effect, and K the dynamic constant associated with such properties of the system as the heat capacity, the cooling rate, etc.

As a matter of fact that A times E is the heat flow rate detected by the calorimeter at any time, let h represent $A\cdot E$, Eq. (1) becomes:

$$H = h + K\,\frac{dh}{dt} \qquad (2)$$

On the other hand, the heat flow rate H generated by an electrode reaction is related with the current, the electrode potential, etc. according to the following Eq. [7]:

$$H \pm \varphi_i(VS\ \mathrm{SHE})I = \frac{I}{zF}\cdot{}''\Delta_rH_{m,i}{}'' - R_i\cdot I^2\ (+i = a,\ -i = c) \qquad (3)$$

where the footnote i denotes the anodic reaction $(i=a)$ or the cathodic reaction $(i=c)$, I the current $(I>0)$, φ_i the electrode potential $vs.$ the standard hydrogen electrode, $''\Delta_rH_{m,i}''$ the apparent molar enthalpy change of the electrode reaction, R_i the effective electrical resistance of the anode or the cathode compartment, z the stoichiometric coefficient of electron in the reaction, and F the Faraday constant. Substituting Eq. (3) into Eq. (2), one obtained:

$$K\,\frac{dh}{dt} + h = \pm(-\varphi_i I) + \frac{I}{zF}\cdot{}''\Delta_rH_{m,i}{}'' - R_i\cdot I^2 \qquad (4)$$

Equation (4) is the mathematical–physical equation concerning the electrode reaction taking place in the calorimeter at a certain temperature.

Equation (4) can be solved within two separate periods:

First, within the electrochemical polarization, $t=0$ to $t=t_n$, the solution of Eq. (4) is:

$$\frac{Khe^{t/K} \pm \int \varphi_i I e^{t/K}dt}{\int I e^{t/K}dt} = \frac{''\Delta_rH_{m,i}''}{zF} - \frac{\int I^2 e^{t/K}dt}{\int I e^{t/k}dt}\cdot R_i \qquad (5)$$

Equation (5) is integrated from zero to $t(t\leq t_n)$. For simplification, Eq. (5) may also be rewritten as:

$$y = \frac{''\Delta_r H_{m,i}''}{zF} - R_i \cdot x \qquad (6)$$

where y and x in Eq. (6) represents the corresponding terms in Eq. (5).

Second, when the electrochemical polarization terminates, $t \geq t_n$, the solution of Eq. (4) is:

$$h = [h(t_n) \cdot e^{t_n/K}] e^{-t/K} = h'(t_n) \cdot e^{-t/K} \qquad (7)$$

or

$$\ln h = \text{constant} - \frac{1}{K} \cdot t \qquad (8)$$

consequently, K can be figured out by regression with Eq. (8) with the data in the 'natural cooling' period in the thermogram, and then y and x can be calculated by digital integrations with the data in the period of the electrochemical polarization in the thermogram. The desired apparent enthalpy change $''\Delta_r H_{m,i}''$ then can be obtained by regression with Eq. (6).

Experimental

It is suggested by observing Eq. (6) that in order to obtain $''\Delta_r H_{m,i}''$ with little regression error, x and thus y should be able to change within fairly wide regions. Since x is mainly related with the current I at any time, as shown by Eq. (5), the linear sweep–current polarization for calorimetry is appropriate for the purpose. In the present work, the anodic process of the electrode system 0.1 mol/l $[Fe(CN)_6]^{4-}$ + 0.1 mol/l $[Fe(CN)_6]^{3-}$ (saturated with KCl) was chosen for the preliminary calorimetric determination under linear sweep–current polarization.

Apparatus used in the present work was a set–up combining a microcalorimeter (Setaram HT1000) with the usual electrochemical instruments, as shown in Fig. 1. The standard resistance for current determination was one of high precision (0.01%). The sensitivity of the calorimeter was calibrated by Joule effect, and the digital voltmeters measuring the electrode potential and current were calibrated with a standard Weston cell and a potentiometer.

After thermal stabilization, the electrode system was polarized under anodic linear sweep–current by the potentiostat. The anodic oxidation of ferrocyanide to ferricyanide took place:
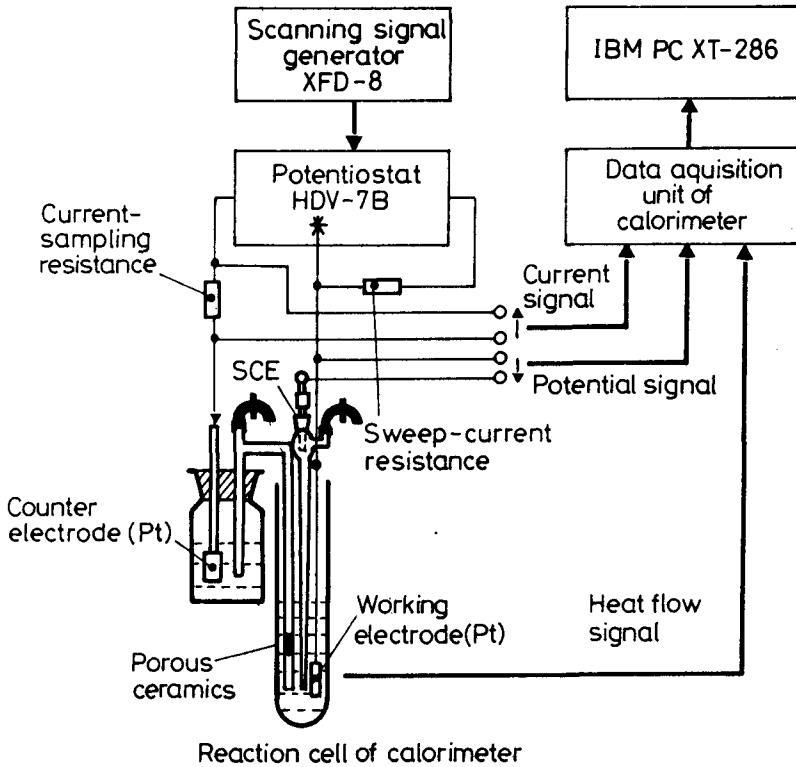
$$[Fe(CN)_6]^{4-} - e = [Fe(CN)_6]^{3-} \qquad (9)$$
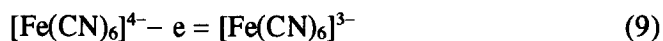
Fig. 1 The set-up for calorimetry under linear sweep–current polarization

The anodic potential φ_a, the current I and the heat flow h were all collected simultaneously by an IBM PC XT-286 microcomputer with the software THEL [8]. The experimental record is shown in Fig. 2. Data were stored in a floppy disk for data processing.

Results and discussion

A computer program written in Quick Basic language was used to calculate the dynamic constant K with Eq. (8), and then to calculate y and x in Eq. (6) at any time. K obtained was 227 s. Curve of y vs. x is shown in Fig. 3. Very good linear relationship between y and x exists, as shown by the regression line in Fig. 3.

$$10y = 9.8140 - 0.4072(10x)$$

Therefore, $''\Delta_r H_{m,i}''/1 \cdot F = 0.9814$, or $''\Delta_r H_{m,i}'' = 0.9814 \times 96485 = 94690$ J/mol = 94.7 kJ/mol.

In our previous work [4], calorimetric study of the same electrode system under a series of constant−current polarization were made. The apparent enthalpy change was 90.5 kJ/mol. It is seen that the apparent enthalpy change in the present work is in good agreement with this value, which proves that the established mathematical−physical equation and its solutions can describe the real measurement fairly well.
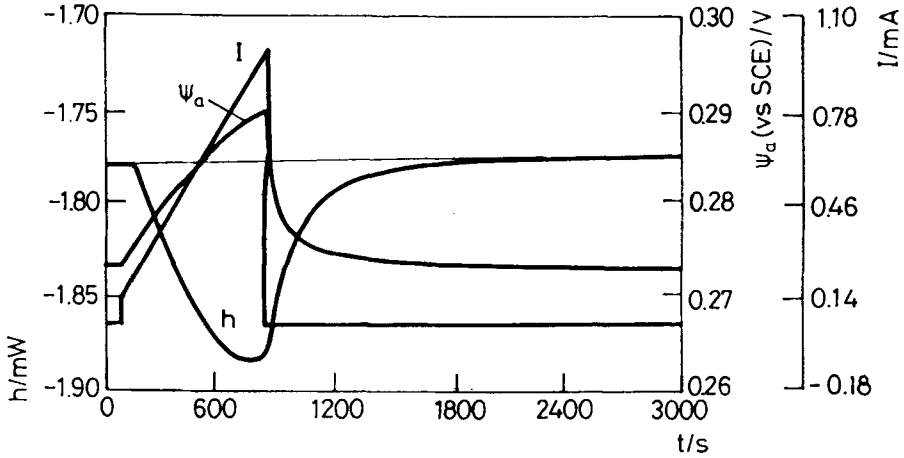
Fig. 2 Calorimetry record, current sweeping rate 1.2×10^{-3} mA/s, temperature 25.8°C
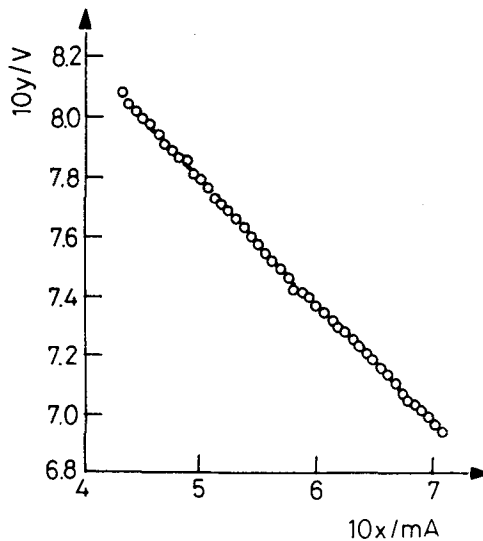
Fig. 3 Curve of y vs. x

Other current sweeping rates and electrode systems are now under research to improve the method developed in the present work.

Conclusions

1) The mathematical–physical equation for an electrode reaction taking place in a heat-conducting calorimeter at a certain temperature was derived, and its solutions were obtained for the polarization period and the natural cooling period respectively.

2) Usual electrochemical instruments were combined with the microcalorimeter to study the calorimetry of an electrode reaction under linear sweep–current polarization.

3) The results of the calorimetric determinations of the anodic process of the ferro- and ferri-cyanide system with the linear sweep–current method coincide with those of the constant–current method. Thus the developed method is applicable for rapid determination of apparent enthalpy change of an electrode reaction.

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Zusammenfassung — Es wurde die mathematisch-physikalische Gleichung für den Kalorimetrievorgang von Elektrodenreaktionen hergeleitet und die entsprechenden Lösungen für die Periode der elektrochemischen Polarisierung und für die des natürlichen Abkühlens erhalten. Die Kalorimetrie der anodischen Oxidation von Hexazyanoferrat(II) zu Hexazyanoferrat(III) bei linearer Kippstrompolarisierung wurde ausgeführt, die erhaltene scheinbare Enthalpieänderung der Elektrodenreaktion stimmte gut mit der bei der Kalorimetrie mit konstantem Strom überein. Die entwickelte Kalorimetrie bei linearem Kippstrom und die Datenauswertungsmethode können für eine schnelle Bestimmung der scheinbaren Enthalpieänderungen von Elektrodenreaktionen verwendet werden.