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INVESTIGATION ON MICROELECTRODES
XII THE DETERMINATION OF THE INVERSE CURRENT IN THE PROCESSES OF STEADY-STATE OR QUASI-STEADY-STATE

Hueng Xian JU, Hong Yuan CHEN* and Hong GAO(H.KAO)
Department of Chemistry, Nanjing University, Nanjing 210008, China

Abstract: *A simple method for determining the inverse current of cyclic voltammetry in the processes of steady–state or quasi–steady–state was presented. The experimental result verified the theoretical relation of inverse and forward current at microelectrode. Their ratio is proportional to the square root of scan rate.*

Due to the strong edge effect on microelectrode, the electrode process quickly arrives at steady–state. When the scan rate is slow enough, the forward sweep curve and the backward sweep curve of the cyclic voltammogram overlap each other, and with the increase of scan rate, the two curves will be slightly non–coincident, with the forward current being larger, at a given potential, than the backward current [1]. This is because the electrode process in the backward sweep contains two electrode reactions, i.e. forward and inverse electrode reactions. The total current is composed of the current i_f of positive reaction and i_r of inverse reaction, Galus et al [2] advanced the relation of the two currents:

$$i_f / i_r = 1+QD^{1/2}(RT / nFvr^2)^{1/2} \qquad (1)$$

Where Q is a constant, about 0.92 for usual electrode, v scan rate of potential, D diffusion coefficient, r the radius of electrode, the others are of conventional significance. They had only determined the currents at conventional electrode and in the process of fast sweep by means of the method of Nicholson and Shain's method, and verified partly formula (1). Zoski et al [1] suggested that the discrepancy between I_a and I_c depends on the magnitude of the parameter $2(nFvr^2 / RTD)^{1/2}$, and presented the theoretical relation between the two currents. However, up to date nobody has verified these relations and determined such a small inverse reaction current at microelectrode in the process of steady–state or quasi–steady–state at various scan rate yet, and even considered impossible to measure the i_r at microelectrode [2]. In this work, a simple method for determining the inverse current of cyclic voltammetry was proposed, the experimental results further verified the relation mentioned above.

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* *To whom correspondence should be addressed.*

PRINCIPLE

At microdisk electrode with the radius of r, the steady–state limiting current of single sweep voltammetry for a reversible reaction $R \rightleftharpoons O + ne$ is [3] :

$$i_d = 4nFDC_R^* r \qquad (2)$$

and the currents can be obtained with the first Fick's law and the concept of diffusion layer:

$$I_{f(E)} = KnFD_R(C_R^* - C_R^s) / r \qquad (3)$$

$$I_{r(E)} = -KnFD_O C_O^s / r \qquad (4)$$

Where C_R^* is the bulk concentration of depolarizer, O is oxidation state, R is reduction state, C_O^s, and C_R^s are the concentration of O or R respectively on the surface of electrode when the inverse or forward electrode reaction occurs. At low scan rate, the total currents both in the first forward and the first backward sweep are the sum of Faradaic current and capacitance current:

$$I_{a(E)} = I_{f(E)} + I_{z(E)} \qquad (5)$$

$$I_{c(E)} = I_{f(E)} + I_{r(E)} + {}_{z(E)} \qquad (6)$$

where $I_{z(E)}$ is the charging current, it is much smaller than Faradaic current because of the very small area of microelectrode (The area is 8×10^{-7} cm^2 as the radius is 5μm), and can be neglected. At the same potential, $I_{f(E)}$ of forward reaction can be determined from the forward sweep curve of the cyclic voltammogram first obtained and formula (5), thus, the difference of $I_{a(E)}$ and $I_{c(E)}$ is the current of inverse reaction $i_{r(E)}$.

EXPERIMENTAL

INSTRUMENTAL

A three–electrode configuration was employed. The carbon fiber microelectrode(CFME) with a radius of 5μm was used as the working electrode. SCE with double salt bridge which consisted of saturated KCl solution and 0.1mol/L $N(C_4H_9)_4ClO_4$ acetonitrile solution as the reference electrode. A Pt wire was used as the counter electrode. Experiments were carried out in the acetonitrile solution of 1.3×10^{-3}mol/L ferrocene with 0.1mol/L $N(C_4H_9)_4ClO_4$ as supporting electrolyte under an inert atmosphere of nitrogen.

Voltammetric measurements were made with Polarecord E506, VA–Scanner E612(Switzerland), and 3036 Type X–Y recorder (Yokogawa Hokushin, Tokyo and Sichun, China). Jw–0.001°C Type thermostat(Chongqing Instrument Factory, China).

CHEMICALS

Acetonitrile(C.P.) was redistilled. $N(C_4H_9)_4ClO_4$ was synthesized from $N(C_4H_9)_4Br$(A.R.) and $HClO_4$(A.R.). Ferrocene was of analytical grade reagent.

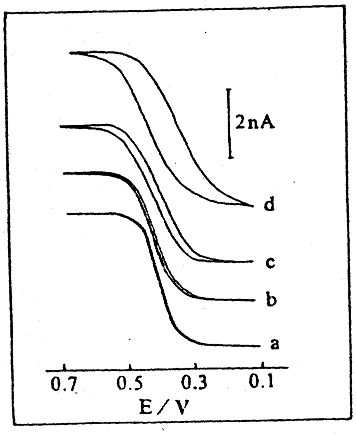
RESULTS AND DISCUSSIONS

1. The cyclic voltammogram at carbon fiber microdisk electrode

It can be seen from Fig.1 that the sigmoidal shape curves in forward sweep and backward sweep of the cyclic voltammetry at carbon fiber microdisk electrode overlap under the condition of low scan rate. With the increase of scan rate, the two curves separate gradually resulted from the inverse reaction current of ferrocene at microdisk electrode.

2. The inverse current at microdisk electrode

The inverse current $I_{r(E)}$ was determined from formula (5) and formula (6). The inverse reaction currents of ferrocene at microdisk electrode at various scan rates and various potentials are shown in Table 1. The result indicates that with the increase of scan rate, the inverse currents increase, and the maximum values of them occur at the half-wave potential at various scan rates. This is in agreement with the theoretical result of eqn.(52) in literature[1]. It is because the product O formed in forward electrode reaction partly and constantly diffuses into the solution in the course of sweep, the product O concentration reserved at electrode surface is C_O^s, during the beginning of backward sweep, C_O^s is the largest, whereas the reduction rate is yet minimum due to the more positive potential, so $I_{r(E)}$ is very small. With the potential moving to more negative value, C_O^s reduces with an exponentially increasing reduction rate,



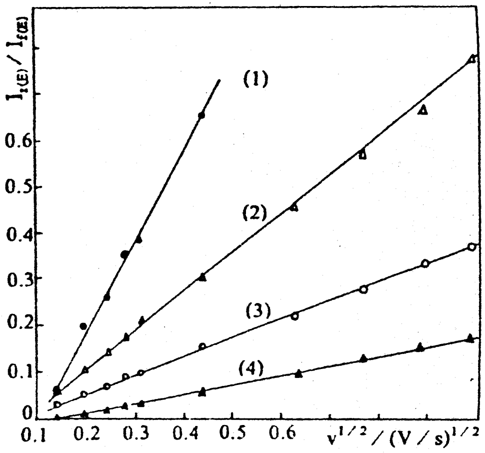


Fig.1 The cyclic voltammogram at carbon fiber microdisk electrode with a)v = 5, b)v = 100, c)v = 400, and d)v = 800 mV / s.

Fig.2 The relationship between $I_{r(E)}/I_{f(E)}$ and $v^{1/2}$ with (1)0.40V, (2)0.45V, (3)0.35V and (4)0.50V.

thus, the reduction current $I_{r(B)}$ increases until arriving at half–wave potential. After passing through the half–wave potential, although the reaction rate increases, the inverse current is going to be lower than that at half–wave potential since C_O^s is getting very small and so far as to tend to zero. While the scan rate increases, the inverse current increases because the amount of yielded product O per unit–time increases with the increase of scan rate, that is, C_O^s increases.

Table 1 The determination of inverse current $I_{r(B)}$

scan rate mV/s E (E)	5	20	40	60	80	100	200	400	600	800	1000
0.30	0.000	0.013	0.019	0.028	0.042	0.045	0.068	0.087	0.167	0.223	0.334
0.35	0.000	0.031	0.123	0.131	0.185	0.199	0.340	0.537	0.695	0.738	0.958
0.40	0.000	0.117	0.216	0.297	0.376	0.499	0.638	0.961	1.20	1.39	1.66
0.45	0.000	0.105	0.197	0.246	0.329	0.363	0.568	0.808	1.02	1.26	1.40
0.50	0.000	0.016	0.033	0.071	0.108	0.119	0.221	0.380	0.556	0.638	0.750
0.55	0.000	0.003	0.010	0.033	0.048	0.056	0.070	0.118	0.200	0.278	0.408
0.60	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.016	0.037	0.089

3. The dependence of inverse current on scan rate

When r is very small, the first item of formula (1) may be neglected, then, the I_r / I_f is proportional to $rv^{1/2}$. When other conditions are fixed, the ratio value is proportional to $v^{1/2}$. The similar relation was given in literature[1]. In Fig.2, the relation was experimentally verified. The slope of this curve is related to potential, and the experimental slope of the curve at half–wave potential is 0.84, it is very close to the theoretical value 0.88 obtained from formula (1) for ferrocene($D = 2.4 \times 10^{-5} cm^2 / s$) at microdisk electrode with the radius of 5μm. Thus, the formula (1) was fully examined experimentally, and the method for determining inverse current is available.

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REFERENCES

1 C.G.Zoski, A.M.Bond C.L.Colyer, J.C.Myland, K.B.Oldham, J.Electroanal. Chem., 1989;263:1

2 Z.Galus, J.O.Schenk, R.N.Adams, J.Electroanal.Chem., 1982;135:1

3 K.Aoki, K.Akimto, K.Tokuda, H.Matsuda, J.Osteryoung, J.Electroanal. Chem., 1984;171:219

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