BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2761—2766 (1970)

Mechanism of Redox Surface Reaction between Wüstite and CO_2 or CO

Seiichi KURIHARA, Kazuo FUEKI, Takashi MUKAIBO and Yasuo WADA

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received April 25, 1970)

The redox reaction between thin wüstite foil and CO_2 or CO was studied by means of a microbalance in a temperature range 900—1075°C. It was found that the reaction at the gas-wüstite interface is rate-controlling and that the reaction rate is expressed as

$$V_{\mathrm{ox}} = k_{\mathrm{O}} P_{\mathrm{CO_2}} a_{\mathrm{O}}^{-m/3} \quad \text{and} \quad V_{\mathrm{red}} = k_{\mathrm{O}}' P_{\mathrm{CO}} a_{\mathrm{O}}^{n/3},$$

where a_{O} is the oxygen activity of wüstite, and m and n are 2.1—2.2 and 0.8—1.2, respectively. On the basis of the theory by Kobayashi and Wagner, the most predominant mechanism is concluded to be

$$CO_2 + 2\ominus \rightleftarrows CO + O^{2-}$$

Actigation energies for k_{O} and k_{O}' were 35+3 and 32+3 kcal/mol, respectively.

In the redox reaction at the gas-solid interface, chemical species in the solid phase take part in the reaction as well as gaseous reactants. Therefore, in order to elucidate the reaction mechanism, it is necessary to determine the reaction rate as a function not only of the partial pressure of reactant gases but also of the activity of chemical species in the solid phase. Kobayashi and Wagner[1] constructed electrochemical cells, such as Ag|AgI|Ag_2S|Pt and Cu|CuI|Cu_2S|Pt, and measured the rate of reduction of the sulfides by hydrogen under the controlled metal activity by using the coulometric titration technique. They also proposed a new theory whereby the experimental results can be explained. Thereafter, new experimental techniques such as the isotopic exchange method[2,3] and the chemical relaxation method[4] have been developed in addition to the coulometric titration technique.

Grabke[2] has studied the exchange reaction between $^{14}CO_2$ and ^{12}CO on the wüstite surface at 800—985°C and found that the exchange rate is a function not only of the partial pressures of CO_2 and CO but also of the oxygen activity of wüstite. He has also discussed the reaction mechanism on the basis of the Kobayashi-Wagner theory.

In order to investigate the mechanism of the reaction at the gas-solid interface, we have devised

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[1] H. Kobayashi and C. Wagner, *J. Chem. Phys.*, **26**, 1609 (1957).

[2] H. J. Grabke, *Ber. Bunsenges, Physik. Chem.*, **60**, 48, (1965).

[3] K. Fueki, H. Inaba and T. Mukaibo, This Bulletin, **43**, 23 (1970).

[4] S. Stotz, *Ber. Bunsenges, Physik. Chem.*, **70**, 37 (1966).

a new technique which uses a microbalance and studied the redox reaction between wüstite and CO_2 or CO. The purpose of the present paper is to report the result of the study.

Experimental

a) Principle of Microgravimetric Technique. Wüstite is a metal-deficit type nonstoichiometric compound and often expressed by the chemical formula $Fe_{1-\delta}O$. The equilibrium relation between δ and $a_O(\equiv P_{CO_2}/P_{CO})$ has been determined precisely by Darken and Gurry⁵⁾ and by other investigators.⁶⁾ According to the result of their thermodynamic investigations, the homogeneous nonstoichiometric range of wüstite is fairly wide, for instance, δ ranges from 0.05—0.15 at 1000°C. Thus, the change in δ within the stable region of wüstite can be followed gravimetrically.

According to a study of iron oxidation in CO_2–CO gas mixtures,⁷⁾ the oxidation is controlled by the gas-oxide interface reaction in the initial period of oxidation where the oxide scale is thin. Therefore in the case of oxidation and reduction of wüstite, the overall reaction is expected to be controlled by the reaction on the wüstite surface, if the wüstite specimen is sufficiently thin. In such a case, the surface reaction rate can be obtained by measuring the weight change of wüstite as a function of time. When the reaction is controlled by the surface reaction, δ is constant throughout the specimen. Thus, the value of δ of wüstite at every moment can be determined by following the weight change during the run. Since there is a close relationship between δ and a , we can determine the surface reaction rate as a function of a_O.

b) Apparatus. Figure 1 shows a schematic diagram of the apparatus. The reaction tube (A) was a mullite tube, 3.6 cm in inner diameter and 72 cm long, to which upper and lower glass tubes were connected by glass joints. The upper glass tube (B) was connected to a stainless steel inner tube (C). The outer tube (D) which was also made of stainless steel, can be raised or lowered together with the balance chamber (E) above it. In order to secure a vacuum seal, an O-ring (F) was inserted between the outer stainless steel tube and the inner one. Gas was passed upward through the reaction tube. The furnace (G) was wound with Kantal wire. The temperature gradient was less than 0.2 deg/cm over the region where the specimen (H) subjected to reaction. Temperature was controlled by means of an electronic controller within +1.5°C and measured by a calibrated Pt-Pt.Rh thermocouple (I). The weight change of wüstite specimen was followed continuously by means of Cahn RG electrobalance (J).

c) Purification of Gases. CO_2 was passed successively through a $Mg(ClO_4)_2$ column and an activated copper column to remove water vapor and oxygen. CO was passed through $Mg(ClO_4)_2$ to remove water vapor and then through an activated copper column to convert O_2 into CO_2, which was absorbed in a soda lime column.

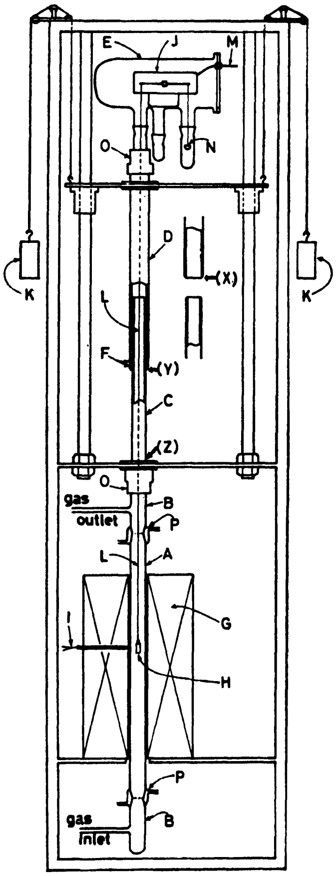

Fig. 1. Schematic diagram of the apparatus.
A: reaction tube (Mullite), B: glass tube, C: stainless steel inner tube, D: stainless steel outer tube, E: balance chamber, F: O-ring, G: furnace, H: specimen, I: thermocouple J: Cahn's RG electrobalance, K: weight, L: silica fibre, M: electric cable, N: counter weight, O: glass/stainless tube junction, P: water jacket to cool the glass/Mullite junction region.

d) Preparation of Wüstite Specimen. Wüstite specimens were prepared as follows. A rectangular coupon, approximately 1.2 cm long by 0.8 cm wide was taken from a sheet of electrolytic iron 0.14 mm thick. Results of spectroscopic analysis is shown in Table 1. A hole, 1 mm in diameter was drilled near one end of the coupon and the coupon was washed with soap and water, rinsed in alcohol, dried in a desiccator and weighed. A Pt hock was then attached through the hole. After the outer tube (D) was raised to position X so as to be detached from the inner one, the coupon was suspended from the balance with a silica fibre. The outer tube was then lowered to position Y and the reaction apparatus was evacuated. After evacuation CO_2 was admitted to the system and let to flow at a flow rate of 20 cc/min. The outer tube was then lowered to position Z in order to oxidize the iron specimen at 1050°C. When the weight reached the

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5) L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, **67**, 1398 (1945).

6) I. Bransky and A. Z. Hed, *J. Amer. Ceram. Soc.*, **51** (4), 231 (1968).

7) F. S. Pettit and J. B. Wagner, Jr., *Acta Met.*, **12**, 35 (1964).

Table 1. Spectroscopic analysis of electrolytic iron

Impurity	Content (ppm)	Impurity	Content (ppm)
Ni	150	Cr	10
CO	130	Si	10
Zn	110	Al	5
Mo	50	Mg	5
Cu	30	V	1
Mn	20	Pb	nil
Ca	16	B	nil

value corresponding to the nearly stoichiometric ratio of iron to oxygen, the oxidized specimen was raised from the hot zone by raising the outer tube to position Y and the furnace temperature was changed to the desired reaction temperature. Then the reaction apparatus was evacuated and a CO_2–CO mixture whose CO_2/CO ratio was 2/3 was introduced to the system. The oxidized specimen was lowered to the furnace and equilibrated with the gas mixture at the reaction temperature. When the weight became constant, the metal deficit, δ, was calculated from the weight change the specimen before and after oxidation. Data of the present work agreed well with Darken's. The thickness of wüstite specimen was about 0.3 mm and the average grain size was about 100 μ.

e) Measurement of Surface Reaction Rate. After the reaction apparatus was evacuated, CO_2 gas desired partial pressure was introduced to the system to oxidize the wüstite. Since the length of time needed for the introduction of gas was less than 15 sec, weight change during the introduction was negligibly small. Thus, the value of $\log a$ of wüstite at the beginning of oxidation was thought to be equal to $\log 2/3$. When the weight of the specimen reached the value corresponding to $\log a = 0.6$, CO_2 was removed from the system to stop the oxidation, and CO of desired partial pressure was introduced to initiate the reduction. In this way, the same wüstite specimen was used repeatedly for the kinetic measurement of oxidation in CO_2 and reduction in CO at desired partial pressures in a range of $\log a_O = -0.18$—0.6. The wüstite specimen was kept in the furnace during the kinetic measurement to prevent the wüstite specimen from decomposing by quenching, since the wüstite phase is unstable below 570°C. After repetition of oxidation and reduction, a gas mixture of $P_{CO}/P_{CO} = 2/3$ was introduced into the reaction apparatus to equilibrate the wüstite specimen with the gas mixture. A comparison of the equilibrium weight at the end of the run with that at the beginning showed the difference between the two weights to be less than 10% of the total weight change of the oxidation or reduction of wüstite.

The measurement was carried out in a temperature range 950—1075°C and at pressures of 70—300 mmHg.

Results

Typical oxidation curves of wüstite in CO_2 and reduction curves in CO are shown in Figs. 2 and 3. respectively. In these figures the scale of δ is also given. The wüstite specimen employed in this experiment was so thin that the overall reaction is supposed to be controlled by the surface reaction. It is thought that the gradient of δ is not formed in the specimen, and the surface reaction rate, V, at a specified value of δ is determined from the slope of tangent drawn to the curve at the δ value. Since there is a relationship between the oxygen activity in wüstite (a_0) and δ, the relationship between V and a_0 is determined.

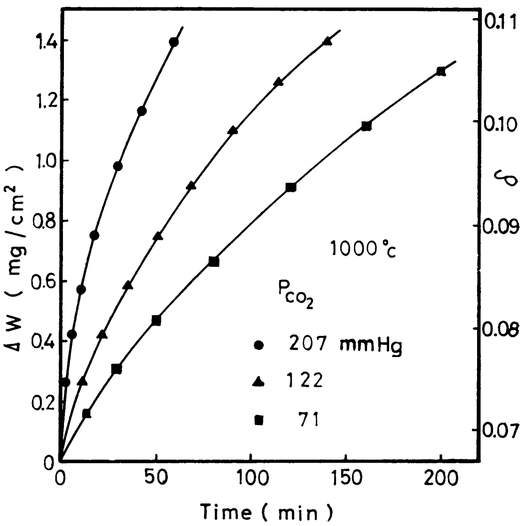

Fig. 2. Oxidation curves of wüstite by CO_2.

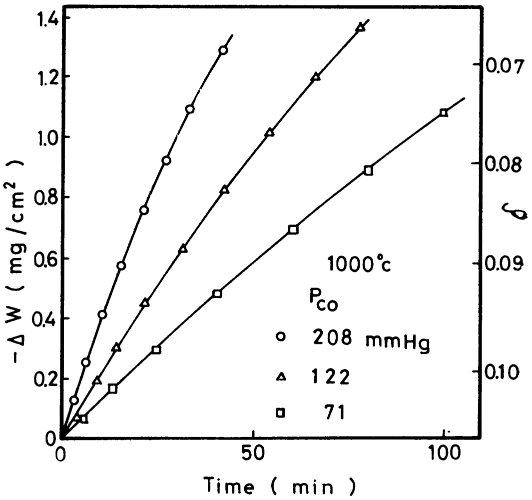

Fig. 3. Reduction curves of wüstite by CO.

Figure 4 shows the plots of $\log V$ *vs.* $\log a_O$. In the case of reduction, the plots of $\log V$ *vs.* $\log a_0$ show a good linearity. In the case of oxidation, an abnormally high rate was observed in the initial period of oxidation, especially at high pressures of CO_2. However, even in such cases the reduction performed immediately after the oxidation showed no abnormality. At low CO_2 pressures,

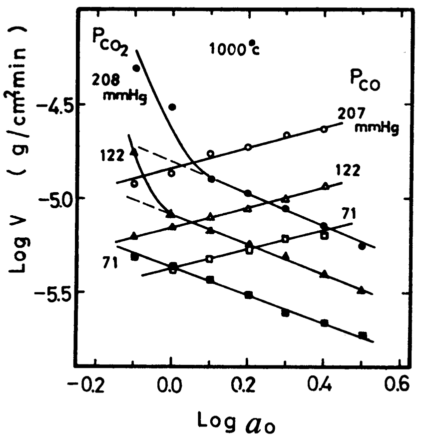

Fig. 4. Relationship between V and a_O.

the plots of log V *vs.* log a_0 give a good linearity. The cause of abnormally high rate of oxidation has not been elucidated yet.

Figures 5 and 6 show the dependence of V on partial pressures of CO_2 and CO at constant a_0, respectively. V linearly depends on gas pressures. This clearly shows that the overall reaction is controlled by the reaction at the surface.

Accordingly, the rate of oxidation, V_{red}, and the rate of reduction, V_{red}, are expressed in terms of P_{CO_2}, P_{CO} and a_O as follows:

$$V_{ox} = k_O P_{CO_2} a_O^{-m/3} \tag{1}$$

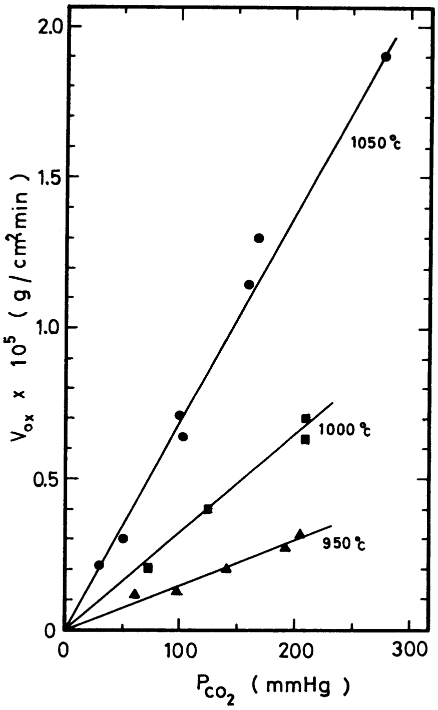

Fig. 5. Dependence of oxidation rate, V_{ox}, on partial pressure of CO_2, P_{CO_2} at $a_O = 25$.

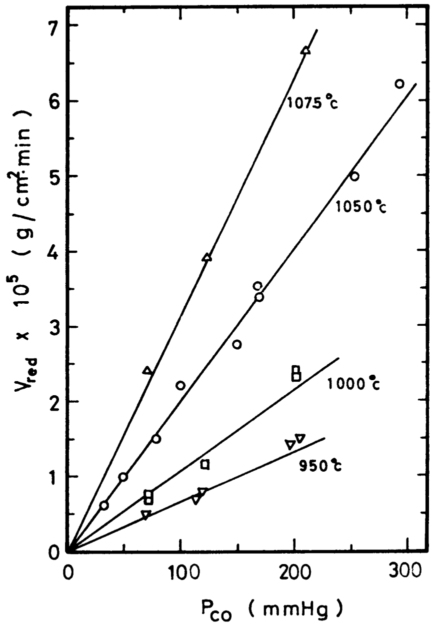

Fig. 6. Dependence of reduction rate, V_{red}, on partial pressure of CO, P_{CO} at $a_O = 25$.

$$V_{red} = k_O' P_{CO} a_O^{n/3} \tag{2}$$

The values of m and n at various temperatures are listed in Table 2. It is noteworthy that m is approximately 2 and n is approximately 1. Rate constants k_O and k_O' defined in Eqs. (1) and (2) were obtained by extrapolating the linear relationship in Figs. 5 and 6 to the gas pressure of 1 atm. and substituting 2.5 for a_O. The Arrhenius plots of k_O and k_O' obtained in this way are shown in Fig. 7. From the definition of $a_O \equiv P_{CO_2}/P_{CO}$ and the equilibrium condition, $V_{ox} = V_{red}$, k_O and k_O' should be equal to each other. However, as seen in Fig. 7, a discrepancy of about 25% exists between k_O and k_O'. In the case of oxidation, experimental results showed a rather large deviation at high pressures of CO_2. Therefore, the value of k_O is thought to be less accurate than the value of k_O'. Activation energy for k_O and k_O' are $35.0+3$ kcal/mol and 33.0 ± 3 kcal/mol, respectively. Grabke[2] found 33.5 ± 2 kcal/mol as the activation energy of of dissociative adsorption of CO_2 on wüstite in the kinetic study of isotopic exchange between $^{14}CO_2$ and ^{12}CO at temperatures from 800°C to 983°C.

TABLE 2. VALUES OF *m* AND *n*

Temp. (°C)	*m*	*n*
950	2.1	1.2
975	2.1	1.1
1000	2.2	1.3
1025	2.1	0.9
1050	2.2	1.2
1075	—	0.8

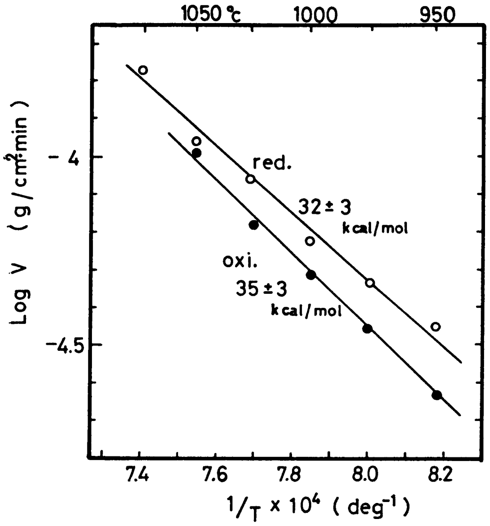

Fig. 7. Arrhenius plots of k_O and k'_O.

The present activation energy is nearly the same as Grabke's.

Discussion

The reaction mechanism can be discussed on the basis of the Kobayashi-Wagner theory as follows. The reaction between CO_2 and CO on the wüstite surface proceeds by the parallel reactions

$$CO_2 \rightleftarrows CO + O \tag{3.A}$$

$$CO_2 + \ominus \rightleftarrows CO + O^- \tag{3.B}$$

$$CO_2 + 2\ominus \rightleftarrows CO + O^{2-} \tag{8.C}$$

where O, O^-, and O^{2-} represent adsorbed oxygen atoms, monovalent oxygen ions and divalent oxygen ions, respectively, and $\ominus$ electrons in wüstite.

Assuming that the adsorbed oxygen atoms and oxygen ions are in equilibrium with those in bulk of wüstite and that the adsorption of CO_2 and CO is weak, we can write the rate equations as

$$V_A = k_1 P_{CO_2} - k_1' P_{CO} a_O \tag{4.A}$$

$$V_B = k_2 P_{CO_2} a_\ominus - k_2' P_{CO} a_{O^-} \tag{4.B}$$

$$V_C = k_3 P_{CO_2} a_\ominus{}^2 - k_3' P_{CO} a_{O^{2-}} \tag{4.G}$$

where a_O, a_{O-}, $a_{O^{2-}}$ and $a_\ominus$ denote the activities of respective species.

Assuming the equilibrium among posititive holes ($\oplus$), cation vacancies ($Fe_\square{}''$) and oxygen atoms in wüstite, we obtain

$$O \rightleftarrows FeO + Fe_\square{}'' + 2\oplus$$

$$\frac{a_{Fe_\square{}''} a_{\ominus^2}}{a_O} = k_1 \tag{5}$$

Because of the low concentration of $Fe_\square{}''$ and $\oplus$, we have

$$x_{Fe_\square{}''} \approx a_{Fe} \tag{6}$$

$$x_\oplus \approx a_\oplus \tag{7}$$

where x denotes the concentration.

From the charge neutrality condition

$$2x_{Fe_\square{}''} = x_\oplus \tag{8}$$

it follows that

$$a_\oplus = K_2 a^{1/3} \tag{9}$$

Other equilibrium conditions and mass action laws are

$$\ominus + \oplus \rightleftarrows \text{Null}$$

$$a_\ominus \cdot a_\oplus = K_3 \tag{10}$$

$$O^- \rightleftarrows O + \ominus$$

$$a_O \cdot a_\ominus = K_4 a_{O^-} \tag{11}$$

$$O^{2-} \rightleftarrows O + 2\ominus$$

$$a_O \cdot a_{\ominus^2} = = K_5 a_{O^{2-}} \tag{12}$$

Combination of Eqs. (9), (10), (11) and (12) yields

$$a_\ominus = K_6 a_O{}^{-1/3}$$

$$a_{O^-} = K_7 a_O{}^{2/3} \tag{14}$$

$$a_{O^{2-}} = K_8 a_O{}^{1/3} \tag{15}$$

Inserting these equations into Eqs. (4.A)—(4.C), we obtain

$$V_A = k_1 P_{CO_2} - k_1' P_{CO} \tag{16.A}$$

$$V_B = k_2 K_6 P_{CO_2} a_O{}^{-1/3} - k_2' K_7 P_{CO} a_O{}^{2/3} \tag{16.B}$$

$$V_C = k_3 K_6{}^2 P_{CO_2} a^{-2/3} - k_3' K_8 P_{CO} a_O{}^{1/3} \tag{16.C}$$

The generalized rate equation is

$$V = k_O P_{CO_2} a_O{}^{-m/3} - k_O' P_{CO} a_O{}^{3/n} \tag{17}$$

where m and n are integers characteristic of reaction mechanism as listed in Table 3. The first term on the right side represents the oxidation rate of wüstite by CO_2 and the second term represents the reduction rate of wüstite by CO, namely,

Table 3. PREDOMINANT REACTION MECHANISM AND VALUES OF m AND n

Mechanism	m	n
(A) $CO_2(ads) \rightleftarrows CO(ads) + O(ads)$	0	3
(B) $CO_2(ads) + \ominus \rightleftarrows$ $CO(ads) + O^-(ads)$	1	2
(C) $CO_2(ads) + 2\ominus \rightleftarrows$ $CO(ads) + O^{2-}(ads)$	2	1

$$V_{ox} = k_O P_{CO_2} a^{-m/3} \tag{18}$$

$$V_{red} = k_O' P_{CO} a_O{}^{n/3} \tag{19}$$

In the present work, values of m and n were determined experimentally, so we can conclude the predominant mechanism of the three. From a comparison of Tables 2 and 3 it is concluded that the most predominant mechanism of the surface reaction is

$$CO_2 + 2\ominus \rightleftarrows CO + O^{2-}$$

Summary

(1) Oxidation of wüstite by CO_2 and reduction by CO in a homogeneous range of wüstite were

studied kinetically by the microgravimetric method. The reactions were found to be controlled by gas-oxide interface reaction.

(2) The surface reaction rate was determined as a function of gas pressure and oxygen activity in wüstite, a_O, in a temperature range 950—1075°C at pressures of 70—300 mmHg.

(3) The oxidation rate in CO_2 and reduction rate in CO were expressed respectively as

$$V_{ox} = k_O P_{CO_2} a^{-m/3} \qquad (m = 2.1\text{—}2.2)$$

$$V_{red} = k_O' P_{CO} a_O^{n/3} \qquad (n = 0.8\text{—}1.2)$$

(4) Activation energies for rate constants k_O and k_O' were 35±3 kcal/mol and 32±3 kcal/mol respectively and coincided with those obtained by Grabke.

(5) From Wagner's theory the predominant mechanism was determined as the two electron transfer mechanism:

$$CO_2 + 2\ominus \rightleftarrows CO + O^{2-}$$

Support by Takeda Science Foundation is gratefully acknowledged.