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Electrochemical Oxidation of Carbon Monoxide in Aqueous Solutions

E.I.Konnik

The advances achieved recently in the electrochemical oxidation of carbon monoxide, which is a comparatively cheap fuel for electrochemical generators (fuel cells), are considered and the problems of the further improvement of the electrochemical oxidation of carbon monoxide are analysed. The electrochemical methods for the analysis of carbon monoxide, which are important for industry, medicine, and scientific research, are reviewed.
The bibliography includes 32 references.

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1. INTRODUCTION

The electrochemical oxidation of carbon monoxide has been the subject of study for a long time. Together with the hydrogen and hydrazine electrodes, the carbon monoxide electrode as well as electrodes comprising hydrocarbons and other organic compounds as reducing agents are of great interest as negative electrodes in current sources and in other fields of applied electrochemistry.

However, whereas the improvement of the hydrogen electrode, by K.Kordesch, F.T.Bacon, E.Justi and coworkers, R.Kh.Burshtein and coworkers, and others, has led to a considerable increase of the current generated by porous catalytic hydrogen electrodes, the improvement of the carbon monoxide electrode has been less satisfactory.

The reversible thermodynamic potential of carbon monoxide is much more negative than that of the hydrogen electrode, particularly in 5 M KOH where it is -1580 mV at 25°C relative to the saturated calomel electrode, i.e. more negative by 450 mV than the reversible hydrogen electrode in the same solution (Justi et al.[1], p. 244). The e.m.f. of a system comprising this electrode and a reversible oxygen electrode should be 1680 mV under these conditions. However, the steady-state potential of the carbon monoxide electrode attainable at present is between only -1210 and -1230 mV.

The use of the carbon monoxide electrode in current sources appeared unpromising until recently. The rate of electrochemical oxidation of carbon monoxide on smooth metal electrodes was so low that the current generated at a moderate polarisation amounted to a few microamperes per cm^2 of the true surface. This caused workers in the 1940s and 1950s to attempt to use the carbon monoxide electrode in current sources at 700 to 900°C.[2,3] Moreover, the life of such a cell did not exceed several days and the current density at an acceptable polarisation was a few mA cm^{-2}; as shown below, the use of high temperatures is thermodynamically unfavourable.

2. THERMODYNAMIC PRINCIPLES AND HISTORY OF THE ELECTROCHEMICAL OXIDATION OF CARBON MONOXIDE

In studies on the thermodynamics of the electrochemical oxidation of carbon monoxide, one uses as the cathodic process the electrochemical reduction of oxygen, the characteristics of which at catalyst electrodes made of different materials are now being vigorously investigated in connection with the development of fuel cells employing different types of fuel. Thus the electrochemical system consists of the galvanic cell

$$^{-}\mathrm{CO} \mid \text{electrolyte} \mid \mathrm{O_2} + \qquad (1)$$

At constant pressure, the maximum amount of energy which may be obtained from an electrochemical current source is equal to the [decrease of the] free energy $-\Delta G$ of the reaction, described by the Gibbs–Helmholtz equation

$$-\Delta G = -\Delta H + T\Delta S = zFE\,, \qquad (2)$$

where ΔH is the change in the enthalpy of the system as a result of the reaction, T the absolute temperature, ΔS the change in the entropy of the system as a result of the reaction, z the number of electrons involved in the electrochemical reaction, E the e.m.f. of the current source, and F the Faraday.

Since the heat of reaction $Q = -\Delta H$, it follows that

$$zFE = Q + T\Delta S \qquad (3)$$

and further $E = Q/zF + T(\partial E/\partial T)_p$, where $(\partial E/\partial T)_p = \Delta S/zF$ is the temperature coefficient of the e.m.f.

According to Eqn.(3), the e.m.f. depends not only on the heat of the reaction in the current source, but also on the entropy term $T\Delta S = TzF(\partial E/\partial T)_p$. If $(\partial E/\partial T)_p > 0$ (the entropy increases so that $\Delta S > 0$), the e.m.f. increases with temperature.

The entropy change is equal to the difference between the entropies of the reaction products and the initial reactants:

$$\Delta S = \Sigma n_i S_{i_{prod}} - \Sigma n_i S_{i_{start}} \quad (4)$$

where n_i is the number of moles of the ith reactant.

The molar entropies of gaseous elements and many gaseous compounds differ little from one another and are considerably higher than the entropies of liquid and solid substances. In other words, since the degree of disorder in it is highest, the gas phase makes the greatest contribution to the entropies. Therefore $\Delta S > 0$ if the number of moles of the gaseous reaction products $n_{g.prod}$ is greater than the number of moles of the gaseous starting materials.

If $n_{g.prod} < n_{g.init}$, then $\Delta S < 0$, $(\partial E/\partial T)_p < 0$, and the e.m.f. decreases with temperature. If $n_{g.init} = n_{g.prod}$, then $\Delta S \simeq 0$, $(\partial E/\partial T)_p \simeq 0$, and the e.m.f. hardly depends on temperature, as, for example, the e.m.f. of the current source in which the following reactions take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,$$
$$C + O_2 \rightarrow CO_2 .$$

For the reaction $2CO + O_2 \rightarrow 2CO_2$, $n_{g.prod} < n_{g.init}$ and therefore the e.m.f. of the current source in which carbon monoxide is oxidised electrochemically by oxygen decreases with temperature, as can be seen from Fig. 1 which includes for comparison the temperature dependence of the e.m.f. of the hydrogen–oxygen cell.

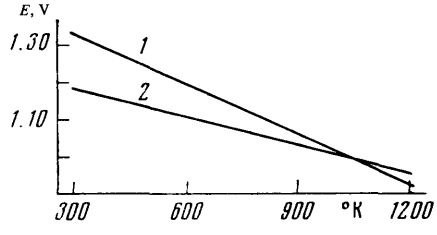


Figure 1. Temperature variation of the e.m.f.'s of gas cells: 1) carbon monoxide–oxygen cell; 2) hydrogen–oxygen cell.

The maximum (ideal) efficiency in the complete electrochemical oxidation of the fuel is

$$\eta = \frac{-\Delta G}{-\Delta H} ,$$

whence, using Eqns. (2) and (3), we obtain

$$\eta = 1 + T \cdot \frac{\Delta S}{Q} . \quad (5)$$

It is evident from Eqn. (5) that η may be greater than unity (i.e. greater than 100%) for a reaction with $\Delta S > 0$ ($n_{g.prod} > n_{g.init}$). In this case, the operation of the current source involves the removal of heat $\Delta Q = T\Delta S$ from the surrounding medium and its transformation into electrical energy. The cell itself does not become cold.

For example, a current source of this type would be one in which electrochemical oxidation of carbon occurs: $2C + O_2 \rightarrow 2CO$ (incomplete combustion of carbon).

In the electrochemical oxidation of carbon monoxide, $\Delta S < 0$, so that η of cell (1) decreases with temperature. This is evident from Table 1, which includes for comparison also data for the hydrogen–oxygen cell (Justi et al.[1], p. 32).

Thus the use of the carbon monoxide electrode in an electrochemical cell at a low temperature (not exceeding 100°C) under the conditions employed to develop active electrodes is more promising than at high temperatures, as was suggested at one time by Davtyan[2] and Daniel' Bek et al.[3] and comparatively recently by Chambers and Tantram[4].

Table 1.

Reaction	Z	T° K 300		600		900		1200		$\left(\frac{\partial E}{\partial T}\right)_p \cdot 10^3$
		E	η	E	η	E	η	E	η	
$2CO + O_2 \rightarrow 2CO_2$	4	1.33	0.91	1.2	0.81	1.06	0.72	0.92	0.63	0.445
$2H_2 + O_2 \rightarrow 2H_2O$	4	1.18	0.94	1.1	0.88	1.03	0.80	0.95	0.73	0.255

Justi and Grüneberg and coworkers, as well as other electrochemists including Soviet workers, have contributed to recent advances in the low-temperature electrochemical oxidation of carbon monoxide. One of the first attempts to employ the carbon monoxide electrode was in the Borchers cell (1894) (Davtyan[5], p. 39):

$$-CO\,(Cu)\,|\,HCl,\,CuCl\,|\,(Cu)\,O_2^+ . \quad (6)$$

Borchers suggested that the electrodes were involved in the following reactions:

At the anode	At the cathode
$2Cl^- \rightarrow Cl_2 + 2e$,	$2Cu^{2+} + 2e \rightarrow 2Cu^+$,
$Cl_2 + CO_{soln.} + H_2O \rightarrow CO_2 + 2H^+ + 2Cl^-$	$^1/_2O_2 + 2Cu^+ + 2H^+ \rightarrow 2Cu^{2+} + H_2O$.
Overall process:	Overall process:
$CO_{soln.} + H_2O \rightarrow CO_2 + 2H^+ + 2e$.	$^1/_2O_2 + 2H^+ + 2e \rightarrow H_2O$.

However, the insignificant e.m.f. of this cell could not be due, according to some investigators, to the above reactions. Mond (Davtyan[5], p. 39) suggested that the e.m.f. of the Borchers cell is due to the electrodes employed. He justified this hypothesis by the fact that the replacement of the copper electrodes in the Borchers cell by carbon electrodes reduces the e.m.f. almost to zero. No data are available for the potential of the Borchers cell when the current is drawn to an external circuit.

More successful was the Hofmann cell[6,7]:

$$-\,CO\,(Cu)\,|\,KOH\,|\,(CuO,\,Cu)\,O_2\,^+ . \quad (7)$$

Here the potential close to that of the reversible hydrogen electrode is established at the copper|carbon monoxide electrode and Hofmann noted that this electrode gives a higher current for the same polarisation if the material of the electrode is partly in a carbon monoxide atmosphere (the idea which found a practical application in porous electrodes). The e.m.f. of this cell was 1.04 V, increasing to 1.17 V when platinum was employed as the material of the positive electrode. Apart from a fairly high e.m.f., another advantage of this cell when the electrode materials

described are employed is the use of an alkaline electrolyte in which copper is much more stable than in the electrolyte of the Borchers cell [cell (6)] and the rate of electrochemical reduction of oxygen is much higher. However, cell (7) suffers from the disadvantage that its electrolyte reacts with the product of the reaction.

3. KINETICS AND MECHANISM OF THE DIRECT ELECTROCHEMICAL OXIDATION OF CARBON MONOXIDE

Direct low-temperature electrochemical oxidation of carbon monoxide has been investigated at Group IB and VIII metals and also at tungsten, rhenium, and molybdenum. The electrodes were both smooth and porous (Raney type catalysts made of these metals were employed).

Table 2.

Electrode material	Soln. composition	Temp., °C	Steady-state potential on open circuit, mV: rel. to normal hydrogen electrode	Steady-state potential on open circuit, mV: rel. to hydrogen electrode in same soln.	Current density, mA per cm^{-2} of apparent surface	Polarisation, mV	References
Pt	0,1N H_2SO_4	25	—	+160	0.1	700	8
Pd	1,0N H_2SO_4	80	—	+85	—	—	9
Platinised Pt.	1N H_2SO_4	10—15	—	+170	—	—	10
Pt	ditto	30	—	00	—	—	10
Pt-DSC*	3N H_2SO_4	100	—	00	50	100	11
ditto	ditto	100	—	00	200	300	11
Pt	2N H_2SO_4	25	+360	—	—	—	12
Pt	1N $HClO_4$	25	—	—	4	800	18

*Double-skeleton catalyst electrode with a Raney platinum catalyst and a supporting framework made of gold powder (CO pressure 1.5 atm).

a. Acid Solutions

The experimental data available at present for the steady-state potentials of the carbon monoxide electrode made of different metals and their behaviour under the conditions of anodic polarisation are presented in Table 2 (the partial pressure of carbon monoxide is 1 atm throughout).

Almost all the few available data concerning sulphuric acid solutions demonstrate the difficulty of devising a carbon monoxide electrode in acid solutions. This is shown firstly by the finding that between 10° and 80°C the steady-state potential at platinum and palladium and platinised platinum electrodes not only does not approach the value for the reversible carbon monoxide electrode but does not even reach the potential of the reversible hydrogen electrode in this solution (Table 2). The only exception are data obtained recently by a group of German electrochemists for Pt-DSC † electrodes [11]. Secondly, this is indicated by the polarisation characteristics of the carbon monoxide electrodes made of these metals. At a smooth platinum electrode, an appreciable rate of electrochemical oxidation of carbon monoxide (about 0.1 mA cm^{-2}) is achieved only at a potential of 850–900 mV [8] and reaches a maximum (about 1 mA cm^{-2}) at a potential of 1000–1100 mV. The current depends both on the potential of the electrode (the state of its surface) and on the diffusion flux of carbon monoxide. On further increase of the potential, the current falls almost to zero owing to the passivation of the electrode by oxygen.

Recent data concerning the electrochemical oxidation of carbon monoxide in 3 N sulphuric acid are of considerable interest for the formation of a highly active carbon monoxide electrode at low temperatures [11]. The authors employed DSC electrodes about 1 mm thick comprising a Raney platinum catalyst. The steady-state potential of the carbon monoxide electrode measured at 100°C was 0.0 mV (Table 2), i.e. was more positive than the reversible carbon monoxide electrode only by 132 mV, while in experiments [1] in 5 N KOH (85°C) using Raney molybdenum as a catalyst, the steady-state potential was more positive than that of the reversible carbon monoxide electrode by 370 mV.

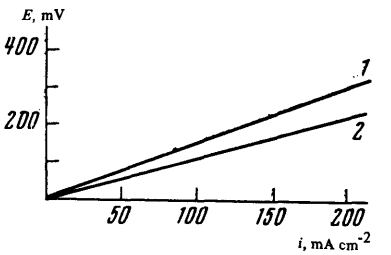


Figure 2. Steady-state polarisation characteristics of platinum DSC electrodes at 100°C (potentials given relative to the hydrogen electrode in the same solution): 1) carbon monoxide as depolariser; 2) hydrogen as depolariser.

Fig. 2 presents the steady-state polarisation characteristics for the electrochemical oxidation of carbon monoxide and hydrogen at a Pt–DSC electrode [11]. Evidently the rate of electrochemical oxidation of carbon monoxide at this electrode is fully comparable to the rate of electrochemical oxidation of hydrogen under these conditions for a not much higher polarisation. The polarisation characteristics of this Pt–DSC electrode in the electrochemical

† A double-skeleton catalyst electrode (Ed. of Translation).

oxidation of carbon monoxide are much better than in the electrochemical oxidation of hydrocarbons such as methane, ethane, and ethylene. Thus the kinetic parameters available at present for the carbon monoxide electrode in acid solutions are satisfactory.

The process mechanism has been considered by many investigators, who established that the carbon monoxide adsorbed on platinum and palladium exists in two forms (Young [13], p. 30; Fasman et al. [14]): a bridge form (8a) and a less stable linear form (8b).



(8a)



(8b)

Carbon monoxide is adsorbed when the *d* shell of the metal contains unfilled levels [15] and the greater the number of *d* vacancies the more stable the adsorption bond. The fraction of *d* vacancies in palladium is 0.55 per atom [16] and the metal can form fairly stable chemical compounds with carbon monoxide. Their stability depends on the pH: [9] in alkaline solutions, they are less stable and are located on the surface of the electrode, while in acid solutions they penetrate also the crystal lattice of the metal and decompose only at an elevated temperatures.

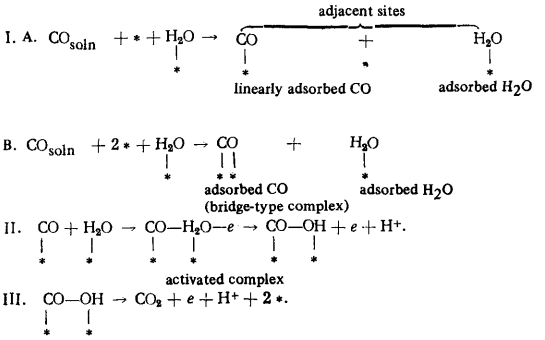
Accordingly, when carbon monoxide is introduced on platinum in 1 *N* sulphuric acid [10] at a potential of 500 mV relative to the hydrogen electrode in the same solution (the so called double layer region) at 50–70°C, the potential shifts to 50–70 mV in 30–60 min. Then it begins to move slowly towards positive values, because at 10–15°C carbon monoxide undergoes physical adsorption and at 20–30°C CO is converted into CO_2 and H_2 by the reaction

$$CO + H_2O \rightarrow CO_2 + H_2 . \qquad (9)$$

At 50–70°C the conversion of carbon monoxide is accompanied by its stable chemisorption (the formation of bridge-type bonds) and the hydrogen formed initially is displaced from the surface of the electrode. Thus at 50–70°C the potential–time curve has a minimum which can be accounted for by the onset of the conversion of carbon monoxide. This is confirmed also by the analysis of the gas phase when the electrode is saturated with carbon monoxide. The maximum carbon dioxide and hydrogen contents were observed precisely at 20–30°C. [10] Similar relations are observed in the adsorption of carbon monoxide on palladium [9,17].

The form of the potential–time curves [10] leads to the conclusion that, in contrast to 1 *N* H_2SO_4, in 1 *N* $HClO_4$ on platinised platinum there is no conversion of CO, since, after the attainment of a steady-state potential, the latter no longer changes in the temperature range 10–50°C. In this case surface compounds with weak and stable bonds are formed.

The mechanism of the step involving the electrochemical oxidation of carbon monoxide in 1 *N* $HClO_4$ at a platinum electrode was investigated by Gilman [18] in a stirred CO-saturated solution through which a triangular potential pulse was applied at a rate of 0.04 V s^{-1} at potentials between 400 and 1800 mV (relative to the hydrogen electrode in the same solution). Up to a potential of 700 mV, the current was very low, reaching a maximum of approximately 4 mA cm^{-2} at a potential of 800 mV. Subsequently the current fell sharply and then increased again only at 1550 mV, owing to the evolution of oxygen. When the potential was varied in the opposite direction, the curve had a different form. Gilman suggests a three-stage mechanism for the electrochemical oxidation of carbon monoxide at a platinum electrode in an acid solution (* — active adsorption centre):



(9a)

According to Gilman stages I (A and B) are very fast whatever the surface coverage not exceeding the equilibrium value, and their rate is determined by that of the diffusion of carbon monoxide. Stage II, which proceeds via the activated complex, determines the rate of electrochemical oxidation of carbon monoxide, which involves weakly adsorbed carbon monoxide. Stage III is fast.

The electrochemical oxidation of carbon monoxide,

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e , \qquad (10)$$

in 2 *N* H_2SO_4 on polished platinum [12] is regarded as chemical oxidation of carbon monoxide by oxygen evolved on the electrode and chemisorbed in the atomic form. The oxygen atoms react rapidly with chemisorbed CO to form CO_2, which is desorbed from the electrode. As a result, platinum is freed for the adsorption of fresh CO molecules and the process mechanism can be represented as follows:

$$\begin{cases} Pt + H_2O \rightarrow Pt{-}O + 2H^+ + 2e , \\ Pt{-}O + Pt{-}CO \rightarrow Pt_2{-}CO_2 , \\ Pt_2{-}CO_2 \rightarrow 2\,Pt + CO_2 . \end{cases} \qquad (11)$$

In the same study [12], it was observed that the electrode potential varies comparatively little when the surface coverage by monoxide falls to zero, as can be seen from the following data:

	CO partial pressure, atm			
	1.0	0.1	0.0037	0.00
CO oxidation potential, mV (relative to the normal hydrogen electrode).	1.25±0.13	1.18±0.11	1.03	1.00±0.11

These data confirm that there is no direct electrochemical oxidation of carbon monoxide, since the potential should change more markedly with decrease of the surface coverage by carbon monoxide. In both investigations [12,18], it was concluded that the carbon monoxide molecule is not involved in electron exchange with the electrode. The difference between them is as follows: Gilman [18] postulates that carbon monoxide is oxidised via an activated complex with water, while Warner and Schuldiner [12] believe that it proceeds via the dissociation and adsorption of oxygen, the adsorption of carbon monoxide, and the chemical reaction between the adsorbed carbon monoxide and atomic oxygen according to Eqn. (11) with subsequent desorption of carbon monoxide.

It is at present difficult to make a well-founded choice between these two mechanisms. Probably the mechanism should depend on the nature of the metal and its capacity to adsorb carbon monoxide and water. The inhomogeneity of the surface of the metal, which involves the possibility that the process may occur via different mechanisms on its different parts, is also important.

The attainment of the hydrogen electrode potential at DSC electrodes [11] led the authors to the hypothesis that carbon monoxide reacts with water to form carbon dioxide and molecular hydrogen. However, under these conditions there is also a possibility of direct electron exchange between carbon monoxide and the electrode metal, since Raney catalysts reduce sharply the activation energy for the reaction. Therefore it may prove unnecessary for the reaction to proceed via an activated complex to reduce the activation energy and also there may be no need for the interaction with the surface oxides on the electrode metal or for the shift of the electrode potential towards positive values up to 1 V and above (relative to the hydrogen electrode in the same solution). The observation of DSC electrode potentials more negative than the reversible hydrogen electrode potential would confirm this possibility.

An important characteristic of platinum and gold electrodes is that in acid solutions (1 *N* $HClO_4$) at potentials in the region of 1.25 V (relative to the hydrogen electrode in the same solution), the electrode surface is poisoned during the oxidation of carbon monoxide at a constant potential [19]. The poisoning is due to the products of the competing electrode reaction involving the oxidation of CO to $(CO)^+$. The (CO^+) cation is removed slowly by electrochemical oxidation and subsequent slow desorption.

The capacity of the starting material to form a non-poisoning rather than a poisoning product is characterised by the selectivity constant S, which, like the rate constant kS for the electrochemical removal of the poison, i.e. $(CO)^+$, depends on the electrode material. According to these parameters, platinum is a better electrode metal than gold. For platinum, $S = 0.9742$ and $kS = 6.61 \times 10^{-2}$ s^{-1} and for gold, $S = 0.9148$ and $kS = 2.3 \times 10^{-4}$. [19]

b. Alkaline Solutions

The experimental data obtained hitherto for the steady-state potentials of carbon monoxide electrodes made of different metals and their behaviour under the conditions of anodic polarisation are presented in Table 3 (the partial carbon monoxide pressure is 1 atm throughout).

The data in Table 3 show that in alkaline solutions it is easier to form a carbon monoxide electrode with satisfactory polarisation characteristics. As in acid solutions, best results were achieved with DSC electrodes.

For a smooth copper electrode in 5 *N* KOH, there is a linear relation between the CO oxidation current and potential when the latter is varied from −100 mV (relative to the hydrogen electrode in the same solution) to 400 mV. [20] Next, anodic dissolution of copper begins and the current rises sharply. The negligible adsorption of hydrogen by the copper electrode leads to virtual absence from the polarisation curve for this electrode of the section corresponding to the oxidation of hydrogen. Moreover, copper has an exceptional hydrogen overvoltage [series (16)] and the probability of the evolution of hydrogen is low even at a potential of −100 mV. However, at a potential of 400 mV, the current density reaches not more than 10 $\mu A\ m^{-2}$, which is very low for such a high polarisation. There are no data for the dependence of the potential and the current on the diffusion flux at a copper electrode.

The rate of electrochemical oxidation of carbon monoxide at a smooth palladium electrode in 5 *N* KOH is very much higher [20]. Up to a potential of 100–120 mV (relative to the hydrogen electrode in the same solution), H_2 is oxidised and then up to a potential of 380–400 mV the oxidation of carbon monoxide takes place. Above this potential, the process reaches the region of the limiting current, which is approximately 150 $\mu A\ cm^{-2}$. At a palladium electrode, the current depends markedly on the diffusion flux.

Among DSC electrodes comprising different Raney catalysts, the most satisfactory electrode is one with a molybdenum catalyst, giving a current of 30 mA cm^{-2} for a polarisation of 130 mV at 83°C, which is comparable with the polarisation characteristic of the Ni–DSC hydrogen electrode (Justi et al. [1], pp. 246, 277).

Table 3.

Electrode material	Soln. composition	Temp., °C	Steady-state potential on open circuit, mV: rel. to calomel electrode	rel. to normal hydrogen electrode	Current density, mA per cm^2 of apparent surface	Current density, mA per cm^2 of apparent surface	Polarisation, mV	References
Ni-DSC*	5*N*KOH	83	−1130	—	—	30	75	
Cu-DSC*	ditto	90	−1170	—	—	50	200	
W-DSC*	»	83	−1210	—	—	5	200	
Mo-DSC*	»	83	−1200	—	—	30	130	
Cu	»	25	—	—	−100	0.01	500	20
Pd	»	25	—	—	−150	0.15	300	20
Pd	»	25	—	—	−150	0 40 (limiting current without stirring)	550	20
Pd	40% K_2CO_3 (pH)	27	—	−570	—	—	—	13
Pt	ditto	27	—	−545	—	—	—	13
Rh	»	27	—	−540	—	—	—	13
Os	»	27	—	−520	—	—	—	13
Ir	»	27	—	−510	—	—	—	13
Ru	»	27	—	−475	—	—	—	13
Re	»	27	—	−469	—	—	—	13
W	»	27	—	−462	—	—	—	13
Cu	»	27	—	−190	—	—	—	13
Au	»	27	—	−150	—	—	—	13
Ni_3S_2	6 *N*KOH	25	—	—	−60			21
Ni_3S_2	ditto	75	—	—	−180	380	380	21

*Double-skeleton catalyst electrode comprising a Raney catalyst made from the given metal (Justi et al. [1], p. 246).

At a new electrode comprising the nickel sulphide (Ni_3S_2) catalyst in 6 *N* KOH, steady-state potentials of −180 and −60 mV at 75° and 25° respectively have been attained [21], these being the most negative values found for alkaline solutions (Table 3). However, they are far from the thermodynamic electrode potentials of the CO/CO_3^{2-} system. At a potential of 200 mV and a partial CO pressure of 1 atm in the same system at 75°C, the current reaches 80 mA per cm^2 of the apparent surface. In 1 M K_2CO_3 + 1 M $KHCO_3$ at 75°C and a potential of 180 mV, the current reaches 0.1 mA cm^{-2}. [21] It is extremely interesting that at the nickel sulphide electrode the oxidation of carbon monoxide is selective and H_2, NH_3, methanol, and formate ions present in solution are not oxidised. Therefore, bearing in mind that at a constant potential the CO electrochemical oxidation current is proportional under these conditions to the carbon monoxide concentration, such an electrode can be used as an indicator in the electrochemical determination of carbon monoxide.

Two mechanisms have been proposed for the electrochemical oxidation of carbon monoxide in alkaline solutions. One of these was proposed by Hofmann, who investigated cell (7), and Grüneberg (Justi et al.[1], p. 243), who studied the process at Cu–DSC and Ni–DSC electrodes in alkaline solutions. According to these investigators, the electrode process proceeds via a preliminary purely chemical stage with subsequent electrochemical oxidation of the hydrogen formed:

$$CO + 2OH^- \rightarrow CO_3^{2-} + 2H_{ads} \quad \text{(chemical stage)}, \qquad (12a)$$

$$2H_{ads} \rightleftarrows 2H^+ + 2e \quad \text{(electrochemical stage)}. \qquad (12b)$$

Grüneberg found that the following reactions can also take place at Ni–DSC electrodes:

$$CO + OH^- \rightarrow HCOO^- \quad \text{(chemical stage)}, \qquad (13a)$$

$$HCOO^- + OH^- \rightarrow CO_3^{2-} + 2H_{ads}$$

$$2H_{ads} \rightleftarrows 2H^+ + 2e \quad \text{(electrochemical stage)}. \qquad (13b)$$

Hofmann and Grüneberg justified these conclusions on the basis of the experimental finding that, when carbon monoxide is passed over Raney nickel and Raney copper electrodes, the latter attain the reversible hydrogen electrode potential to within 20 mV. However, Hofmann and Grüneberg's hypotheses cannot be regarded as convincing, since potentials significantly more negative than the reversible hydrogen electrode value have now been attained at the copper electrode in the same solution (Table 3). Grüneberg's postulate concerning the course of reactions (13a) and (13b) also cannot be regarded as final, since, firstly, the hydrogen electrode potential of the Ni–DSC electrode is established with a low reproducibility and, secondly, the hydrogen overvoltage of this electrode is insignificant. Therefore the slight shift of the potential towards negative values from the reversible hydrogen electrode value causes liberation of hydrogen, which resists this shift. Consequently another mechanism for the electrochemical oxidation of carbon monoxide, proposed by Justi et al.[1] (p. 244) and by Miller et al.[8], which accounts for the fact that the potential of certain metals is more negative than that of the reversible hydrogen electrode (this cannot be explained on the basis of the Hofmann–Grüneberg mechanism), is more likely:

$$CO_{ads} + 2OH^-_{ads} \rightarrow \underset{\downarrow K_2CO_3}{CO_2} + H_2O + 2e \quad . \qquad (14)$$

When the reversible hydrogen electrode potential is attained, the reduction of H^+ ions, the rate of which is determined by the electrode potential and the hydrogen overvoltage of the electrode material, becomes possible together with the oxidation of carbon monoxide. The hydrogen liberated consumes a certain number of electrons, which increases the rate of electrochemical oxidation of carbon monoxide without electrons being given up to the external circuit. This reduces the coefficient of utilisation of carbon monoxide when a carbon monoxide electrode is used in electrochemical cells. Thus, at potentials more negative than the hydrogen electrode potential in the same solution, two reactions [reactions (14) and (15)] take place simultaneously on the electrode:

$$2H^+ + 2e \rightarrow H_2 \rightleftarrows 2H_{ads} \quad . \qquad (15)$$

Reaction (15) is secondary. The hydrogen liberated as a result of this process is adsorbed on the electrode, reducing its capacity to adsorb carbon monoxide and possibly occupying active centres on the electrode surface.

The reversible carbon monoxide electrode potential can be approached only for electrodes with a significant hydrogen overvoltage. It is then necessary to bear in mind the following series of metals in terms of their hydrogen overvoltages (Frumkin et al.[22], p. 154):

$$\underset{\text{increase of hydrogen over voltage}}{\overset{\text{increase of catalytic activity in recombination of H atoms}}{\longleftarrow \quad \text{Pt, Pd, W, Ni, Fe, Ag, Cu, Zu, Sn, Pb} \quad \longrightarrow}} \quad . \qquad (16)$$

Therefore the carbon monoxide electrode potential obtained for palladium, which has a much higher hydrogen overvoltage than platinum (Antropov[23], p. 352), was appreciably more negative than the potential of the reversible hydrogen electrode (Table 3). However this is not easy to achieve and not all the investigators obtained such a potential for palladium[9].

A platinum electrode potential more negative than that of the reversible hydrogen electrode has not been obtained[13]. On the other hand, the steady-state carbon monoxide electrode potentials of copper and gold[24], which have a significant hydrogen overvoltages according to series (16), are closer to the reversible value (Table 3).

Analysis of the literature data shows that, as in acid solutions, a high electrochemical activity in relation to carbon monoxide in alkaline solutions requires that the electrode metal should have unfilled *d* orbitals. The electrode potential of the carbon monoxide electrode (and the free energy to which it is proportional) are approximately proportional to the heat of chemisorption. Therefore a stronger bond between carbon monoxide and the chemisorbing metal (a higher heat of chemisorption) increases the irreversible losses of free energy and decreases the steady-state electrode potential.

Evidently a potential close to that of the hydrogen electrode in the same solution is established for palladium (Table 3, Young[13]), while in more alkaline solutions a still more negative potential, up to −150 mV, is reached (Table 3, Tyurikova[20]).

4. ELECTROCHEMICAL OXIDATION OF CARBON MONOXIDE IN THE PRESENCE OF ELECTRON TRANSFER REAGENTS (VARIABLE-VALENCE IONS) AND OF HOMOGENEOUS CATALYSTS

In the electrochemical oxidation of carbon monoxide, the reaction product is carbon dioxide which is absorbed by the electrolyte in alkaline solutions, decreases the activity of the alkali, and impairs the operation of the carbon monoxide electrode. Therefore the use of acid solutions, where this difficulty is absent, would appear to be more promising. However, the materials for DSC electrodes employed in such solutions are very expensive[11]. The difficulty might be resolved on the basis of recent studies of the electrochemical oxidation of carbon monoxide in acid solutions with the aid of variable-valence ions, which are sometimes referred to as electron transfer reagents. Apart from the sharp increase of the rate of reaction at smooth electrodes, an advantage of this procedure is the possibility avoiding the use of a complex system such as porous electrodes.

The guiding factor in the choice of electron transfer reagents is that the potential of their oxidation-reduction transition should be more positive than that of the reversible hydrogen electrode in the given solution and the redox system should be readily regenerated by carbon monoxide.

The effect of complex salts of palladium(II), rhodium-(III), and platinum(IV) [25] and also of ruthenium(IV), osmium(IV), and iridium(IV) [26] on the kinetics of the reduction of $Cr_2O_7^{2-}$, IO_3^-, Fe^{3+}, $[Fe(CN)_6]^{3-}$, Cu^{2+}, and Sn^{4+} ions by carbon monoxide in the liquid phase has been investigated. The rate of reduction in the presence of the above homogeneous catalysts varies in parallel with the standard oxidation-reduction potentials of the corresponding redox systems. The values of these potentials (E_0) at 25°C are presented in Table 4 (Vetter [27], p. 61).

Table 4.

Redox system	Electrode reaction	E_0, mV (rel. to normal hydrogen electrode)
$Cr^{3+}/Cr_2O_7^{2-}$	$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e$	+1330
I_2/IO_3^-	$^1/_2I_2 + 3H_2O \rightarrow IO_3^- + 6H^+ + 5e$	+1195
Fe^{2+}/Fe^{3+}	$Fe^{2+} \rightarrow Fe^{3+} + e$	+771
$[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e$	+360
Cu^+/Cu^{2+}	$Cu^+ \rightarrow Cu^{2+} + e$	+158
Sn^{2+}/Sn^{4+}	$Sn^{2+} \rightarrow Sn^{4+} + 2e$	+150

Thus the reducible ions investigated can be arranged in the following sequence:

$$\xrightarrow[\text{increase of standard redox potential and of rate of reduction by carbon monoxide}]{Sn^{4+},\ Cu^{2+},\ [Fe(CN)_6]^{3-},\ Fe^{3+},\ IO_3^-,\ Cr_2O_7^{2-}} \quad (17)$$

In terms of their activity, homogeneous catalysts can be arranged in the series $Pd^{2+} > Rh^{3+} > Pt^{4+}$ and the most active catalysts are the acido-complexes of the anion $[PdBr_4]^{2-}$. The rate of reduction by carbon monoxide is proportional to the amount of catalyst at its low concentrations and tends to a limit at high concentrations [25]. An excess of Cl^- ions inhibits the reduction reaction and an excess of Br^- ions accelerates it. In conformity with the laws of chemical kinetics, the experimental rate of reduction of the redox system is directly proportional to the partial pressure of carbon monoxide.

Carbon monoxide is readily adsorbed on copper and palladium. However, the dissolution of copper in acid solutions rules out its employment as the electrode metal. The first studies on the electrochemical oxidation of carbon monoxide at platinum and palladium using the Cu^+/Cu^{2+} redox system are now being made. The mechanism of the anodic process involving the Cu^+/Cu^{2+} system is described by the reaction

$$2CO + 2H_2O + 4Cu^{2+} \rightarrow 4Cu^+ + 2CO_2 + 4H^+ . \quad (18)$$

When this type of electrode is employed together with an oxygen electrode, the following overall reaction takes place at the cathode of the resulting cell:

$$O_2 + 2H_2O + 2e \rightarrow 2H_2O_2 + 2e \rightarrow 4OH^- . \quad (19)$$

The overall process in the carbon monoxide–oxygen electrochemical cell is

$$2CO + 4Cu^{2+} + O_2 \rightarrow 4Cu^+ + 2CO_2 . \quad (20)$$

The amounts of water consumed and formed in reaction (20) are identical. Thus water serves as an agent transferring oxygen from the cathode to the anode. The role of the redox system reduces to the transfer of electrons from the CO molecule to the anode. The redox system is regenerated by oxidation at the anode. The reaction product (carbon dioxide) is removed from the solution as it is formed.

However, the current densities obtained when the Cu^+/Cu^{2+} system is employed amount to several mA cm^{-2}. Such low current densities can be apparently accounted for by the fact that, although the redox system has a sufficiently negative E_0 (Table 4), according to series (17) the rate of reduction of the Cu^{2+} ion by carbon monoxide is low. Moreover, at this current density the electrode potential is markedly displaced towards positive values, which makes this redox system relatively unsuitable for use in electrochemical cells at the present stage of development. It is also necessary to investigate the effect of the Cu^+ and Cu^{2+} additives introduced into the electrolyte on the oxygen electrode.

5. THE PROBLEM OF THE ELECTROLYTE IN THE ELECTROCHEMICAL OXIDATION OF CARBON MONOXIDE

Until comparatively recently, the choice of an electrolyte for the electrochemical oxidation of carbon monoxide involved a vicious circle, which now can be regarded as having been broken. The point is that the rate of electrochemical oxidation of carbon monoxide in acid solutions at smooth electrodes is negligibly low (and porous electrodes have begun to be used only comparatively recently). In alkaline solutions, where not only the rate of electrochemical oxidation of carbon monoxide but also the rate of electrochemical reduction of oxygen is higher, the electrolyte absorbed the carbon dioxide formed, which entails a decrease in the activity of the alkali and impairment of the operation of the carbon monoxide electrode.

This difficulty was partly overcome for alkaline electrolytes by the suggestion of Matusevich and Bagotskii [28], who investigated the effect of carbon dioxide passed through a weakly alkaline electrolyte on the pH of the solution. In such a solution, carbonate and bicarbonate are in equilibrium:

$$CO_3^{2-} + CO_2 + H_2O \rightleftarrows 2HCO_3^- , \quad (21)$$

and the presence of OH^- ions is ensured by the hydrolysis of the bicarbonate. The alkalinity of the solution increases as the equilibrium in reaction (21) shifts to the left with increase of temperature. It was found that at 98°C this type of electrolyte, consisting of $K_2CO_3 + KHCO_3 + H_2O$, at an overall concentration between 3 and 5 N and with constant flow of carbon dioxide, undergoes hardly any change in pH. However, this investigation refers to weakly alkaline solutions (pH not exceeding 10), which are employed comparatively rarely.

It has been stated that Justi and Winsell [29] developed a more promising method involving electrodialysis, whereby the absorption of carbon dioxide by alkali may be prevented. In the operation of a carbon monoxide electrode in an electrochemical cell, not more than 10% of the electrical energy generated by the cell is consumed in the electrodialysis.

A Pd-DSC electrode, which can work in both alkaline and acid solutions [29], has also been developed. In addition there is a Pt-DSC electrode [11] the characteristics of which in acid solutions are not inferior to those of DSC electrodes in alkaline solutions (Table 2). However, in acid solutions both these electrodes have to be made of precious metals, while the DSC electrodes for alkaline solutions require comparatively cheap metals such as nickel, copper, tungsten, and molybdenum.

At present, when the problem of the prevention of the absorption of carbon dioxide by alkaline solutions is close to being solved, the use of alkaline solutions with appropriate DSC electrodes is more justified. However, the future development of DSC electrodes will probably lead to the creation of cheap effective porous electrodes for acid solutions too.

Thus the development of porous electrodes, which has yielded important improvements by accelerating the electrode process and the ways of solving the problem of the electrolyte which have become apparent bring us closer to the achievement of the electrochemical oxidation of carbon monoxide at current densities acceptable in practice.

6. THE APPLICATIONS OF THE CARBON MONOXIDE ELECTRODE

From the very beginning, the carbon monoxide electrode was studied with the aim of its employment in electrochemical cells. The cells proposed by Borchers [5], Hofmann [6,7], Davtyan [2], Daniel' Bek et al. [3], and Chambers and Tantram [4] were of this kind. This is because carbon monoxide is a cheap fuel, which forms part of the gaseous waste from many industrial processes. It can also be obtained by the subterranean gasification of coal.

There has been a particular growth of interest in carbon monoxide electrodes in connection with the problem of fuel cells. The satisfactory results obtained recently in the electrochemical oxidation of carbon monoxide at DSC electrodes in alkaline solutions (Table 3) show that under certain conditions the carbon monoxide electrode is promising as a negative electrode in fuel cells with a weakly alkaline electrolyte.

The studies on the carbon monoxide electrode designed for use in electrochemical cell have created a basis for the development of electrochemical methods for the analytical determination of carbon monoxide. However, their practical application involves many difficulties. One must bear in mind that, when the hydrogen electrode potential in a given solution is attained, the evolution of hydrogen becomes possible. The rate of this process is determined by the electrode potential and the hydrogen overvoltage of the electrode material. The evolution of hydrogen involves the consumption of a certain number of electrons, which increases the rate of electrochemical oxidation of carbon monoxide without transfer of electrons to the external circuit. This may distort the variation of the current or potential with carbon monoxide concentration. If the electrode potential shifts towards values more positive than the hydrogen electrode potential in the given solution, the accumulated adsorbed hydrogen gives rise to an additional anodic current, which also distorts the proportionality between the current and the carbon monoxide concentration. Therefore, for the analytical determination of carbon monoxide, it is particularly necessary to create an electrode at which only the electrochemical oxidation of carbon monoxide would occur. This can be achieved in two ways: by maintaining the electrode potential in the range of values more positive than the hydrogen electrode potential in the given solution or by using an electrode metal with a higher hydrogen overvoltage.

Ovenden [30], who developed an amperometric method for the analytical determination of carbon monoxide at a palladium electrode, followed the first procedure. Moreover, according to series (16), palladium has a higher hydrogen overvoltage than platinum. The experiments were performed at a vibrating steel microelectrode coated with palladium, platinum, rhodium, and iridium at carbon monoxide concentrations in the phase analysed (air) between zero and 100%. The maximum sensitivity (current) and maximum linearity of the variation of the current with carbon monoxide concentration were obtained at palladium, which is the most effective catalyst, among all the metals investigated by Ovenden [30], of the reaction between carbon monoxide and oxygen, in agreement with a number of other data [13,20,29]. The limiting diffusion current at palladium is attained when the potential is between 1.4 and 1.5 V relative to the hydrogen electrode in the same solution. The electrolyte consisted of 0.1 M sodium phosphate (pH 7) and 0.1 M sodium borate (pH 10) buffers and the diffusion coefficients of carbon monoxide in these solutions were found to be respectively 2×10^{-5} and 5×10^{-5} $cm^2\ s^{-1}$. In water, the diffusion coefficient of carbon monoxide is $(2.5 \pm 0.1) \times 10^{-5}$ $cm^2\ s^{-1}$. In the borate buffer [30], the limiting diffusion current was approximately twice as high as in the phosphate buffer, which is due to the difference between the diffusion coefficients of carbon monoxide in these solutions. In the region of the limiting diffusion current in the $CO-O_2$ mixture, the dependence of the current on the carbon monoxide concentration is almost linear at carbon monoxide concentrations between 0 and 100% and independent of electrode polarisation. This shows that in this case the limiting current is fully diffusion-dependent, which is very important for analytical purposes.

Roberts and Sawyer [32], who developed a polarographic method for the determination of carbon monoxide at a gold electrode, which has a high hydrogen overvoltage (Antropov [23], p.352), followed the second procedure. They used spherical and plate electrodes in 0.01 N KOH + 0.1 N K_2SO_4 solution. In the recording of the polarogram at a potential of approximately −500 mV (relative to the saturated calomel electrode), a distinct current peak, controlled by the diffusion of carbon monoxide, was observed. This peak current follows the equation

$$i_p = 3.01 \cdot 10^5 n [n_\alpha (1-\alpha)]^{1/2} A D^{1/2} c v^{1/2} \qquad (22)$$

where n is the number of electrons involved in the electrode reaction, n_α the number of electrons involved in the rate-determining stage of the electrode reaction, A the area of the electrode surface (cm^2), v the rate of increase of potential ($V\ s^{-1}$), c the concentration of carbon monoxide ($mole\ cm^{-3}$), and α the transport coefficient of the electrode process.

The current peak was directly proportional to the carbon monoxide concentration in the range between 0 and 100% in a carbon monoxide–molecular nitrogen mixture, the relation being linear over the entire concentration range investigated. The error of the method is not more than ±2%.

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VODGEO Research Institute,
Moscow