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Copper ion-catalysed electrochemical synthesis of methanol from carbon monoxide on palladium electrodes

Boris I. Podlovchenko* and Tatyana D. Gladysheva

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.
Fax:+ 7 495 939 0171; e-mail: podlov@elch.chem.msu.ru

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The selective electroreduction of CO to MeOH on a Pd electrode in solutions of H_2SO_4 and $CuSO_4$ (in the underpotential region with respect to the Cu^{2+}/Cu couple) is demonstrated for the first time.

The possibility of utilising carbon monoxide through its hydrogenation in the gas phase is thoroughly studied.[1–3] For a long time, insufficient attention was paid to the electroreduction of carbon monoxide,[4–8] which is associated with the high overvoltage of this process, low current efficiencies, and the great number of CO reduction products. Hydrogen was the main product of the cathodic process, while the yield of CO reduction products (methane, ethylene, ethanol, *etc*.) did not exceed 20%. Note that the synthesis of methanol from CO would be the most welcome, the latter being the promising fuel for electrochemical generators.

It was found[9] that carbon monoxide can be electrochemically reduced under mild conditions: at room temperature, atmospheric CO pressure, and in the absence of parallel hydrogen evolution. Such a process was carried out on an iridium electrode in a sulfuric acid solution in the presence of copper ions. However, the greatest part of the passed charge (35–40%) was consumed in the transition from Cu^{2+} to Cu^{+}, whereas the current efficiency in methanol was 8–30%.

Insofar as Pd is known as an active and selective catalyst of liquid-phase hydrogenation,[10] it seemed interesting to study the possibility of CO electroreduction on palladium electrodes under conditions similar to those used previously.[9]

We used electrochemical deposits (e.d.) of Pd applied on smooth polycrystalline platinum (1 cm^2) from solutions of 1 wt% $PdCl_2$ + 0.5 M H_2SO_4 (electrodes I) and 1 wt% $PdCl_2$ + 1 M HCl (electrodes II) at $E = 250$ mV[11] (henceforth, the potentials E are related to the reversible hydrogen electrode in the same solution). The true surface areas of deposits (determined from copper adsorption[12]) ranged from 100 to 150 cm^2.

Polarization and adsorption measurements were performed at 19±1 °C in a three-electrode cell with separated anodic and cathodic compartments. First, a monolayer of copper atoms (Cu_{ad}) was formed on the surface of e.d. Pd in solutions of 0.5 M H_2SO_4 + either 1×10^{-3} or 5×10^{-3} M $CuSO_4$ in the 'underpotential' region at 0.250 and 0.275 V, respectively. Then, CO was flowed through the solution. Upon reaching steady-state currents, a steady-state polarization curve was measured in the potentiostatic mode by varying the potential in the positive direction. In the experiments involving the accumulation of reduction products, the initial potential of either 0.250 or 0.275 V depending on the Cu^{2+} concentration was maintained constant throughout a given sufficiently long time interval (2–6 h). Of all possible products of CO reduction, methanol and folmaldehyde were determined using chromotropic acid.[13] For separately detecting Cu^{+} and Cu^{2+}, bathocuproine was used.[14]

Figure 1 shows that cathodic currents are observed on e.d. Pd throughout a wide underpotential range with respect to the Cu^{2+}/Cu couple, in solutions of H_2SO_4 + $CuSO_4$ + $CO_{saturated}$. It is reasonable to assume that, in the same way as for Ir electrodes,[9] the cathodic currents are due to electroreduction of CO and Cu^{2+}. Insofar as CO and possible reduction products (alcohols, hydrocarbons) are not oxidised on Pd at $E < 0.7$ V, the anodic currents in Figure 1 are apparently the diffusion currents of oxidation of Cu^{+} ions formed.

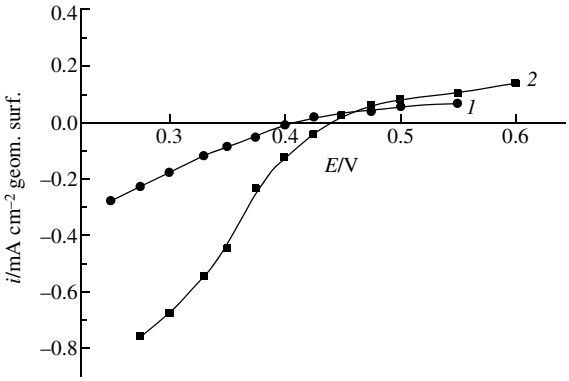

Figure 1 Steady-state polarisation curves in 0.5 M H_2SO_4 + (1–5) M $CuSO_4$ + CO (saturated), on Pd/Pt electrodes I. Concentration of Cu^{2+}: (*1*) 1×10^{-3} and (*2*) 5×10^{-3} mol dm^{-3}.

Table 1 Composition of reduction products at polarization of Pd electrodes I in sulfuric acid solutions containing CO and Cu^{2+} ions ($c_{Cu^{2+}} = 10^{-3}$ M, $E = 0.25$ V). Current efficiences (%) are shown in parentheses.

Q/Q'	c_{Cu^+}/M	c_{HCOH}/M	c_{MeOH}/M
2.0/2	1.8×10^{-4} (14.7)	1.4×10^{-5} (2.8)	1.9×10^{-4} (76)
2.2/2	1.7×10^{-4} (12.5)	1.4×10^{-5} (2.5)	2.5×10^{-4} (88)
0.8/2	5×10^{-5} (12.5)	—	1×10^{-4} (100)

The most interesting results of the analytical detection of reduction products were obtained for electrodes I (Table 1). Q is the charge passed through the electrode and Q' is the charge required for the complete transfer of Cu^{2+} ions present in the solution to Cu^+ (in C). As can be seen in Table 1, methanol is the major product of CO reduction.

On electrodes II, the current efficiencies in MeOH were also significant (30–50%) but substantially lower, as compared with electrodes I. The total yield of Cu^+, H_2CO and MeOH on electrode II was lower than 100%, which points to the formation of other products of CO reduction on these electrodes. The mentioned differences in the behaviours of electrodes I and II suggest that the process is structure-dependent.

On a palladium electrode, the reduction of cations Cu^{2+} to Cu^+ occurs to a lower degree, as compared with iridium electrodes under the same conditions.[9] Nevertheless, Cu^+ ions are present in the solution in concentrations substantially exceeding those calculated using the Nernst equation for the electrode reaction $Cu^{2+} + e \leftrightarrows Cu^+$. This makes it possible to assume that complexes of the $Cu[CO]^+$ type are formed.[9]

The electroreduction of CO at these high potentials (shifted by more than 0.2 V in the positive direction as compared with the hydrogen evolution potentials) should be explained by the catalytic effect of Cu^{2+} ions. The mediator catalysis apparently involves the reduced forms of doubly charged copper ions, which may be represented by both copper adatoms and singly charged copper ions. If we assume that copper adatoms are the intermediate species, the methanol formation can be described by the following equations:

$$2Cu^{2+} + 4e \longrightarrow 2Cu_{ad}$$
$$CO + 2Cu_{ad} + 4H^+ \longrightarrow 2Cu^{2+} + MeOH$$
$$CO + 4H^+ + 4e \longrightarrow MeOH$$

Similar equations can be easily written for Cu^+ or $Cu[CO]^+$ as the intermediate species.

Table 1 indicates that in certain experiments, the overall current efficiency of the reduction products on Pd electrodes I was somewhat higher than 100%. A possible reason for this could be the formation of CO *via* the chemical reaction of CO disproportionation, which proceeds without charge transfer: $3CO + 2H_2O \leftrightarrows 2CO_2 + MeOH$. However, in the numerous experiments, we never observed the total current efficiencies substantially exceeding 100%. In certain experiments, under open circuit conditions, the solutions of $H_2SO_4 + CuSO_4 + CO$ (sat.) were brought into contact with a Pd electrode with a preliminarily accumulated Cu_{ad} monolayer. In the absence of polarization, insignificant amounts of MeOH and HCO were formed. This gives us the grounds to assume that methanol is formed as a result of electroreduction.

Unfortunately, we failed to find published data for the standard potential of the $CO + 4H^+ + 4e = MeOH$ reaction ($E^0_{CO/MeOH}$). However, note that the electrocatalytic formation of MeOH from CO is possible at potentials substantially more positive than $E^0_{CO/MeOH}$ under our conditions: first, initial concentration of methanol is zero and, second, the process of CO reduction runs irreversibly (*i.e.*, CO/MeOH couple is not potential determining).

At present, it is difficult to give preference to univalent copper ions or copper adatoms as the intermediates of the mediator catalysis of CO electroreduction. At the same time, the substantial differences in the rates and products of the processes on electrodes I, II and Ir electrode suggest that they involve the adsorbed copper forms rather than copper ions in solution. Adsorbed forms can represent both copper adatoms and some adsorbed forms of univalent copper ions.

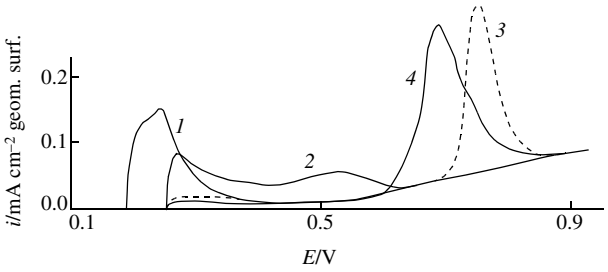

Figure 2 Anodic potentiodynamic curves of Pd/Pt electrode I in 0.5 M H_2SO_4: (*1*) in a supporting electrolyte solution; (*2*) in the presence of a Cu_{ad} monolayer on the surface; (*3*) in the presence of a CO_{ads} monolayer on the surface; (*4*) in the presence of a chemisorption layer formed upon the 4 h cathodic polarisation of the electrode in 0.5 M H_2SO_4 + 1×10^{-3} M $CuSO_4$ + CO (saturated).

The presence of chemisorbed species on the surface of e.d. Pd after its long-term polarization in the working solution was revealed in the experiments in which the electrode was washed with a supporting electrolyte solution (0.5 M H_2SO_4). In the anodic potentiodynamic curve recorded upon CO, its reduction products, and copper ions were removed from the solution bulk, a well pronounced peak of oxidation of the chemisorbed layer is present (Figure 2, curve *4*). Comparing the potential and integral charge of this peak with the corresponding parameters for monolayers of copper adatoms (curve *2*) and adsorbed carbon monoxide (curve *3*) makes it possible to conclude that the peak in curve *4* corresponds to the oxidation of a 'mixed' adsorption layer. The latter includes both the reduced forms of copper (Cu_{ad} and Cu^+) and CO. It was quite unexpected that, at the oxidation of the 'mixed' layer, 1.5–2-times more Cu^{2+} ions passed to solution as compared with the oxidation of a copper adatom monolayer. Probably, multiplayer adsorption takes place. However, this assumption requires special studies, as well as the elucidation of the degree of participation of Cu adatoms, Cu^+ ions, their complexes with CO, and adsorbed individual CO molecules in the formation of a 'mixed' adsorption layer.

Thus, we demonstrated a principal possibility of the electrocatalytic generation of MeOH from CO under mild conditions, namely, on e.d. Pd in sulfuric acid solutions in the presence of Cu^{2+} ions, at room temperature, and in the absence of hydrogen evolution, carbon monoxide can be reduced to MeOH with a current efficiency of ~75%.

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