# Transients of current at the adsorption of carbon monoxide on platinum and palladium electrodes

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**The analysis of the *I vs.* $\tau$ curves obtained during the adsorption of CO on Pt and Pd in 0.5 M $H_2SO_4$ was carried out by using the thermodynamic concept of the electrode total charge.**

Important information on the mechanism of the processes taking place at the contact of electrodes with surface-active substances can be obtained on the basis of the analysis of transients of current (at a constant potential) and potential (at open circuit).[1–3] After CO was brought into contact with Pt and Pd electrodeposits at open circuit potentials stabilised in the double layer region, the potential shifted only in the negative direction.[4,5] This effect was explained by the oxidation of CO. Negative potential shifts at open circuit should correspond to anodic potentiostatic current transients. However, introduction of CO into contact with a single-crystal Pt and polycrystalline smooth platinum at a constant potential $0.3 \le E_r^{ads} \le 0.5$ V[†] in acid solutions led to cathodic current transients.[6,7] The authors explained this by processes of the following type: $Pt^+–A^- + CO + e^- \rightarrow Pt–CO + A^-$ (where $A^-$ is an anion) and assumed that CO is not oxidised at $E_r < 0.5$ V.

Potentiostatic current transients were measured in 0.5 M $H_2SO_4$ after CO was brought into contact with a thin Pd layer electrodeposited on Au.[8] The author observed cathodic currents at $E_r^{ads} > 0.18$ V and anodic currents at $E_r^{ads} < 0.18$ V. This allowed him to conclude that the potential of the zero total charge (pztc) in the presence of $CO_{ads}$ is 0.18 ± 0.02 V.

Thus, the literature data on the form of transients of current and open-circuit potential during the adsorption of CO, as well as their explanation are contradictory. It was interesting to carry out more systematic and comprehensive studies, both theoretical and experimental, of the possibility of using current transients for characterising the adsorption of uncharged species on electrodes of platinum-group metals. The choice of Pt and Pd electrodeposits as the electrode materials was to a large degree caused by the fact that the structure of the electrical double layer is studied sufficiently well on these electrodes and, particularly, their pztc are known.[9–12]

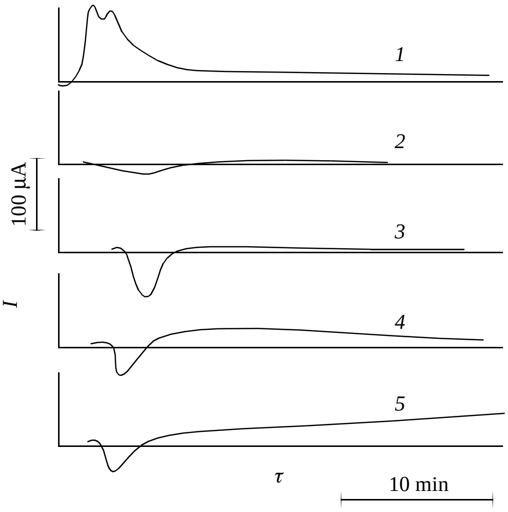

**Figure 1** *I vs.* $\tau$ curves obtained after CO was brought into contact with Pt/Pt under potentiostatic conditions in 0.5 M $H_2SO_4$ at different $E_r$: (*1*) 0.2, (*2*) 0.3, (*3*) 0.4, (*4*) 0.5 and (*5*) 0.6 V.

The electrodeposition of Pt and Pd (5 to 10 mg $cm^{-2}$) was carried out from 2% (w/v) $H_2PtCl_6$ and 1% (w/v) $PdCl_2$ + + 0.5 M $H_2SO_4$ solutions under potentiostatic conditions at $E_r = 0.25$ V.[13,14] The specific surface areas of the deposits ranged from 8 to 18 $m^2\,g^{-1}$. Carbon monoxide contained: CO 99.72 wt%, $CO_2$ 0.23 wt%, $O_2$ and $H_2$ < 10 ppm. For purification of the gas from $CO_2$, we used tubes filled with Ascarite.

The studies were carried out at 18–20 °C in a three-electrode glass cell with separate anodic and cathodic compartments. For measuring potentiostatic transients ($I$–$\tau$ curves), the supporting electrolyte solution was changed for a solution saturated with CO at a fixed potential $E_r^{ads}$ without breaking the circuit (the CO flow through the solution continued).

The thermodynamic theory of the reversible hydrogen electrode developed by Frumkin[9] serves as the theoretical basis for analysing the transients of current when uncharged species are adsorbed in the potential region where they do not undergo any faradaic transformations. If these species are CO molecules, then, during their chemisorption at $E_r^{ads}$ on the metals that reversibly adsorb ions, hydrogen and oxygen, the following relationships should be fulfilled:

$$\Delta Q' = Q'_{CO/M} - Q'_M \qquad (1)$$

$$\Delta Q' = \int_{E^{CO}_{r,Q'=0}}^{E_r^{ads}} C_{CO}\,dE_r - \int_{E^{CO}_{r,Q'=0}}^{E_r^{ads}} C_b\,dE_r, \qquad (1a)$$

where $\Delta Q'$ is the charge consumed in the formation of a $CO_{ads}$ monolayer at a fixed $E_r^{ads}$; $Q'_M$ and $Q'_{CO/M}$ are the total charges of the metal electrode in the absence and in the presence $CO_{ads}$ monolayer on the surface; $C_b$ and $C_{CO}$ are polarisation capacities of the electrode in the supporting electrolyte solution before and after CO adsorption; $E_{r,Q'=0}$ and $E^{CO}_{r,Q'=0}$ are the potentials of the zero total charge in the absence and in the presence of $CO_{ads}$ monolayer.

In potentiostatic transients at $E_r^{ads}$ = 0.4 and 0.5 V (Figure 1, curves *3* and *4*), in the first moment after CO was introduced, the cathodic currents are observed. However, with time, the cathodic currents change to small anodic currents, which suggest slow but quite noticeable electrooxidation of CO on Pt/Pt during the adsorption at the considered potentials (this does not agree with the published data[6,7]). In Figure 1, curve *1* ($E_r^{ads}$ = = 0.2 V), only anodic currents are observed, which, by the large, are determined by the hydrogen displacement from the electrode surface.[3,6,7]

As it follows from expressions (1), if CO is adsorbed as a ‘neutral’ species, zero currents should be observed at those $E_r^{ads}$ at which the electrode total charges in the absence ($Q'_M$) and in the presence ($Q'_{CO/M}$) of $CO_{ads}$ are equal. The potential $E_r = 0.3$ V corresponds approximately to the value $E_{r,Q'=0}$ of a Pt/Pt electrode in 0.5 M $H_2SO_4$.[9] The value $\Delta Q^{cat}$ (Figure 1, curve *2*), which corresponds to $E_r^{ads}$ equal to 0.3 V, is very small, which allows us to suggest that the potential of the zero total charge changes relatively little during the CO chemisorption.[13]

The data obtained lead us to conclude that, in the case of Pt/Pt, the value of $\Delta Q^{cat}$ that corresponds to the current transients at $E_r^{ads}$ of 0.4 V and 0.5 V (Figure 1) is determined not only by displacement of anions from the Pt surface by CO molecules,[6,7]

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[†] The potential values, $E_r$, refer to the reversible hydrogen electrode in the same solution.

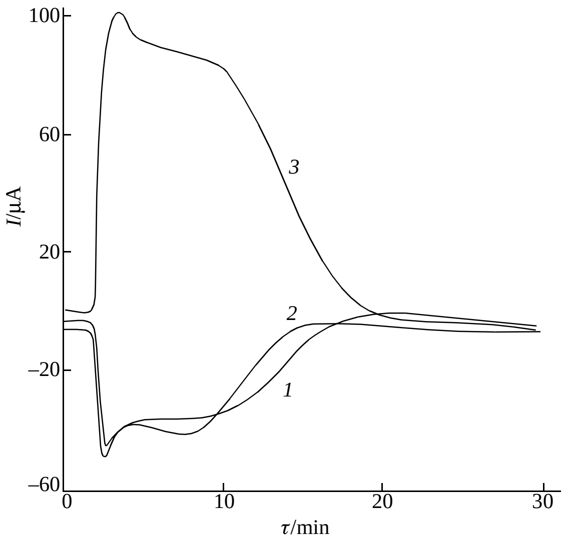

**Figure 2** Potentiostatic current transient measured after CO was introduced into contact with Pd/Pt in 0.5 M $H_2SO_4$ at different $E_\mathrm{r}$: (*1*) 0.65, (*2*) 0.30 and (*3*) 0.09 V.

but also by other processes. Indeed, the capacity value found in the presence of a monolayer of $\mathrm{CO_{ads}}$ on the surface (26 μF cm$^{-2}$) is close to the value of the ionic component of the polarisation capacity of a Pt/Pt electrode in 0.5 M $H_2SO_4$ (35–40 μF cm$^{-2}$).[10] About a half of the total value of the polarisation capacity of Pt/Pt ($C_\mathrm{b}$ = 70–80 μF cm$^{-2}$) falls to adsorbed hydrogen and for oxygen.[9–11] We can conclude that, on Pt/Pt at $E_\mathrm{r}^\mathrm{ads}$ in the ‘double-layer’ region, the decrease in the polarisation capacity and the corresponding cathodic currents observed during the CO adsorption are determined by the displacement of both anions and adsorbed hydrogen and/or oxygen.

Potentiostatic transients measured after CO was brought into contact with a Pd electrode at the potentials of the double-layer region ($E_\mathrm{r}^\mathrm{ads}$ = 0.3–0.65 V) are characterised by pronounced cathodic currents (Figure 2). The charges $\Delta Q^\mathrm{cat}$ that should be passed to the electrode in order to keep the potential constant, calculated per 1 cm$^2$ of the true surface area are vastly greater into absolute value than those of Pt/Pt. The cathodic current drops to zero in 15–20 min and does not change to an anodic current. This allowed us to assume that CO is not noticeably oxidised on Pd at $E_\mathrm{r} \leq 0.65$ V. Hence, the Pd–CO system is more convenient than Pt–CO for the interpretation of the current transients on the basis of the concept of the total electrode charge [see expressions (1) and (1a)].

From galvanostatic curves, we estimated the capacity of electrodeposited Pd in the $E_\mathrm{r}$ interval from 0.4 to 0.8 V in the absence and in the presence of a $\mathrm{CO_{ads}}$ monolayer. The values of $C_\mathrm{b}$ and $C_\mathrm{CO}$ were 33±2 and 9.4±0.4 μF cm$^{-2}$, respectively. The substantial decrease in the capacity of a Pd electrode in the presence of CO, apparently, is associated with a decrease in the dielectric constant of the double layer and an increase in the distance between the ionic plane of the double layer and the metal surface.

If assumed that $Q'_\mathrm{Pd} = 0$ at $E_\mathrm{r} = 0.3$ V,[9,12] by integrating curve *1* in Figure 2, we obtain that the value $Q'_\mathrm{CO/Pd}$ at $E_\mathrm{r}$ = = 0.3 V is 48±4 μC cm$^{-2}$. Such a high absolute value of $Q'_\mathrm{CO/Pd}$ at 0.3 V is only possible if the value of $E^\mathrm{CO}_{\mathrm{r},Q'=0}$ is very high (> 0.8 V).

An alternative way of explaining the cathodic currents when $E_\mathrm{r}^\mathrm{ads}$ is constant may be the assumption of the partial reduction of $\mathrm{CO_{ads}}$ at the double-layer potentials.[8] However, spectral methods did not show any reduced forms of CO on the Pd surface.[14] Moreover, according to our measurements, the values of $\Delta Q'$ in the $E_\mathrm{r}$ interval from 0.3 to 0.65 V did not change with $E_\mathrm{r}^\mathrm{ads}$ within the reproducibility limits. If, as in ref. 8, we assume that the cathodic currents are determined by the formation of reduced forms of $\mathrm{CO_{ads}}$, the independence of $\Delta Q'$ of $E_\mathrm{r}$ is very hard to explain.

Thus, if we consider CO as a neutral species, then the transients of current and $E_\mathrm{r}$ observed suggest that, in the double-layer potential region, the presence of $\mathrm{CO_{ads}}$ changes the sign of the Pd surface charge from positive to negative. Preferential adsorption of anions should change to the preferential adsorption of cations. Probably, this is caused by the adsorption of CO in the form of dipoles oriented with the positive end to the surface. After CO was brought into contact with a Pd/Pt electrode at $E_\mathrm{r}^\mathrm{ads}$ = 0.09 V, substantial anodic currents appeared (Figure 2, curve *3*) which we assumed are due to ionisation of $\mathrm{H_{ads}}$ displaced by chemisorbed CO molecules.

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