IMPEDANCE OF TITANIUM CARBIDE ELECTRODE

I.Paseka

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 250 68 Prague - Řež

The impedance spectra of TiC electrodes were measured in the potential range from -0.6 to $+0.6$ V in $1\text{N-}H_2SO_4$ at ambient temperature. In the region of cathodic hydrogen evolution, the dependence of the imaginary on the real component of the impedance in the complex plane has the form of a half-circle; at potentials more anodic than -0.3 V this dependence is linear. It follows that in the region of hydrogen evolution either no hydrogen is adsorbed on the electrode or the adsorption sites are completely occupied with hydrogen. In the anodic region in the stationary state the electrode is covered with an oxide layer.

Our previous work[1] dealt with the evolution and adsorption of hydrogen on TiC electrodes. It turned out that their behaviour depends appreciably on their history since they are capable of bonding hydrogen after they have been polarized for a sufficiently long time at a cathodic potential $E < -0.6$ V or anodically at $+0.3 < E < +0.8$ V.

Since it follows from the other work[2,3] that an observable decomposition of TiC proceeds at $E > +0.8$ V, it was not clear what processes took place on the electrode in the mentioned anodic potential range. We therefore attempted to elucidate further the behaviour of adsorbed hydrogen in the cathodic potential range and the character of the electrode surface at potentials from -0.3 to $+0.6$ V by measuring the impedance of TiC electrodes.

EXPERIMENTAL

Measurements were carried out with a single-crystal electrode of a composition $TiC_{0.97}$. Its surface was ground prior to measurement with a boron carbide powder and polished with a diamond paste. Solutions were prepared from reagent grade sulphuric acid and triply distilled water and were purified by electrolysis before use with a current of 60 mA for at least 24 h. The electrolyte in the indicator electrode compartment was deaerated by bubbling hydrogen free of oxygen, which continued to bubble during the measurement. The electrode impedance was measured in two ways. At higher frequencies, an impedance bridge of the type R 568 (USSR) with a Wenking RS 61 potentiostat was used. In the range $20-2000$ c.p.s., the impedance was measured by the potentiostat and a sinusoidal a.c. voltage of an amplitude of 3 mV was superimposed upon the d.c. voltage. The real and imaginary components, Z' and Z'', were evaluated from the a.c. current response and the phase angle measured by a phase-meter. All measurements were made after attaining a stationary state where changes of the measured quantities during 30 min were

in the range of experimental errors (about 5%). The frequency-impedance spectrum of the TiC electrodes was measured in the potential range from -0.6 to $+0.6$ V against standard hydrogen electrode on electrodes with a freshly prepared surface as well as on electrodes prepolarized at $+0.5$ V for several hours. By this treatment the electrodes acquired the properties described previously[1].

RESULTS

The impedance diagrams at certain potentials in the complex plane are shown in Figs 1 and 2. It is seen that the impedance diagram at potentials more negative than -0.4 or -0.5 V has the form of a deformed half-circle. The dependence of the impedance on frequency can be expressed in terms of a single capacitive-time parameter τ:

$$Z = R_t / [1 + (j\omega\tau)^\gamma],$$

where R_t is the transfer resistance of the reaction at zero angular frequency ω, and γ is a dispersion parameter[4] whose value was in the range $0.66-0.71$. The values of the d.c. resistance, $R_{ts} = b/2.3I$, at a given potential, where b is the slope of the Tafel line and I direct current were also evaluated (values given in Figs 1 and 2).

At potentials less negative than -0.4 or -0.3 V the frequency-impedance diagram on electrodes ground with boron carbide changes from the half-circular form to a straight line with a slope $dZ''/dZ' \approx 2$; with electrodes polished with the diamond paste to give a mirror-like surface, the dependence of Z'' on Z' is more steep with a slope $dZ''/dZ' \geqq 3.3$ (Fig. 3).

The behaviour of electrodes with a freshly prepared surface differs from the corroded ones at potentials more negative than -0.6 V only in that the current density of hydrogen evolution is somewhat higher in the first case, hence a smaller transfer
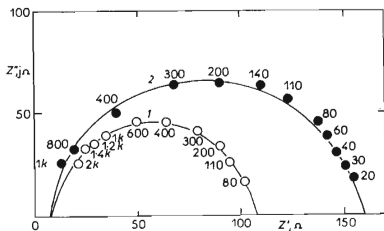

Fig. 1

Impedance Diagram (parameter = frequency in c.p.s.) $E = -0.6$ V

1 Freshly prepared electrode, $R_t = 83$, $R_{ts} = 78$; 2 corroded electrode, $R_t = 152$, $R_{ts} = 164$.

resistance R_t and smaller radius of the circular dependence of Z'' on Z'. At potentials more anodic than -0.6 V, the deformation of the half-circle is much more pronounced on the corroded electrodes than on the fresh ones. Also the value of R_t is somewhat larger in the first case and the transition to the linear $Z'' - Z'$ dependence takes place at more negative potentials.

The values of the series capacity C_s calculated from the measured values of $Z'' = 1/\omega C_s$ were plotted against potential at frequencies of 1.2 and 11 kcps (Fig. 4). In spite of a large scatter it is obvious that the capacity of the TiC electrode is almost independent of potential in the region under study within the range of experimental errors. The dependences of $1/C_s$ on $\log f$ and Z' on $1/f$ were calculated from the impedance spectra at potentials more anodic than -0.2 V. With the polished electrodes, the first relationship was linear in the measured range $(20-1400$ c.p.s.), the second one was linear beginning from 60 c.p.s. and the ratio of the slopes of both

FIG. 2

Impedance Diagram (parameter = frequency in c.p.s.)

1 Freshly prepared electrode, $E = -0.5$ V, $R_t = 430$, $R_{ts} = 430$; 2 corroded electrode, $E = -0.5$ V; 3 freshly prepared electrode, $E = -0.4$ V.

FIG. 3

Impedance Diagram (parameter = frequency in c.p.s.) $E = +0.5$ V

1 Polished electrode; 2 roughly ground electrode.

straight lines was 7·0—9·3. With the nonpolished electrodes, these dependences were not linear in the whole frequency range and the ratio of the slopes of the linear portions of the curves was 11—21, *i.e.* higher.

DISCUSSION

It was found in the previous work[1] that the evolution of hydrogen on freshly prepared TiC electrodes is not accompanied by an observable adsorption of hydrogen. With electrodes subjected to corrosion or hydrogenation processes, however, a certain amount of hydrogen was found in the electrode surface layer. From the theory of the faradaic impedance follows that when the electrode surface is covered with adsorbed hydrogen, relaxation of the coverage Θ_H, introduces an additional time parameter into the expression for the impedance, represented either by a capacitive or by an inductive term[5]. This, however, was found neither with the fresh nor with the corroded TiC electrodes. Hence, in the potential range of hydrogen evolution, between −0·4 and −0·7 V changes in the electrode potential do not cause any change in the surface coverage. This potential independence of the coverage is possible only in two extreme cases: *a)* zero coverage of the electrode with hydrogen ($\Theta_H = 0$), which is possible on a fresh TiC surface, and *b)* full coverage ($\Theta_H = 1$). The amount of bound hydrogen on a corroded electrode at a given potential is, however, not always the same but depends on the history of the electrode[1]. It is therefore necessary to assume that at a given potential all available sites are completely occupied with hydrogen, and if the amount of hydrogen on the electrode changes according to the conditions of measurement it is because the number of the sites capable of bonding hydrogen changes.

In the region of more anodic potentials, $E > −0·3$ V, the linear $Z'' − Z'$ dependence with a slope smaller than 90° can be explained in either of two ways. The
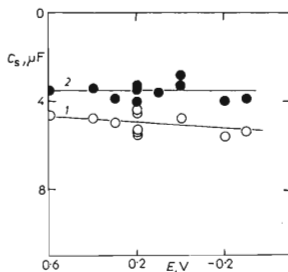

Fig. 4

Relation between Capacity and Electrode Potential

Corroded electrode. *1* $f = 1·2$ kc.p.s.; *2* $f = 11$ kc.p.s.

electrode can be regarded as a capacitor and its impedance corresponds to charging and discharging of the electrode double layer. The slope of the straight line in the complex impedance diagram is due only to dispersion of the capacity caused by roughness of the electrode surface[6]. This is supported by the fact that the slope of the $Z'' - Z'$ line for polished electrodes is greater than for ground ones, the behaviour of fresh electrodes approaching that of an ideal electrode as a capacitor. On the other hand, however, the strongly inhibited course of reduction-oxidation reactions, the existence of a photo-effect in this potential region[1] and the fact that oxidation of hydrogen at anodic potentials proceeds much more slowly than reduction of H_3O^+ ions at cathodic potentials at the same overvoltage show that the electrode surface changes at the anodic potentials and that the impedance behaviour of the TiC electrodes cannot be discussed only in terms of the double-layer impedance. Linear $1/C_s - \log f$ and $Z' - 1/f$ dependences found on polished electrodes are characteristic for the impedance behaviour of oxide layers[7]; the ratio of the slopes of both straight lines approaches also the theoretical value of 9·2. According to Winkel and De Groot[8], such a nonideal capacitive behaviour of a dielectric represented by the oxide layer is caused by the amorphous character of the oxide. Large deviations from the $Z' - 1/f$ linear dependence were measured at frequencies below 60 c.p.s but it can be assumed that the mentioned dependence holds in general only at frequencies above 50 c.p.s. since the published data[7,8] end at this limit. Thus, the overall behaviour of the electrode shows that it becomes covered with an oxide layer at potentials $E \gtreqless -0.3$ V. With roughly ground electrodes, the total impedance involves not only the impedance of the oxide layer but also the capacity dispersion due to roughness of the electrode surface, whereby the nonlinearity of the mentioned dependences for such electrodes can be explained.

The oxide layer formed on titanium carbide at potentials $E \leqq +0.6$ V is, however, somewhat different from the TiO_2 layer formed on titanium[9] or titanium carbide at potentials above 1·0 V (ref.[2]). In contrast to this typically passive layer on which a pronounced dependence of capacity on potential was found, the passive layer formed on TiC at $E \leqq +0.6$ V has a capacity independent of potential. Its composition could not be determined as yet. Instead of the originally assumed[1] composition TiO_{2-x}, it seems more probable that the TiC surface becomes covered with a layer of firmly bound oxygen under formation of an oxycarbide. Whereas titanium electrodes during passivation bind oxygen which at low frequencies behaves as adsorbed oxygen and that only at higher frequencies freezes in the adsorption sites[10] without relaxations in the surface coverage, titanium carbide electrodes bind oxygen in the mentioned potential region in the stationary state so firmly that relaxations in the surface coverage are not observed even at low frequencies.

REFERENCES

1. Paseka I., Balej J.: This Journal *38*, 3600 (1973).
2. Hintermann H. E., Riddiford A. C., Cowling R. D., Malyszko J.: Electrodepos. Surface Treat. *1*, 52 (1972—3).
3. Yonemaya H., Ishikawa Y., Tamura H.: Denki Kagaku *39*, 810 (1971).
4. Epelboin I., Morel P., Takenouti H.: J. Electrochem. Soc. *118*, 1282 (1971).
5. Gerischer H., Mehl W.: Z. Elektrochem. *59*, 1049 (1955).
6. de Levie R.: Electrochim. Acta *10*, 113 (1965).
7. Young L.: *Anodic Oxide Films*. Academic Press, London 1961.
8. Winkel P., de Groot D. G.: Philips Res. Rep. *13*, 489 (1958).
9. Paleolog E. N., Fedotova A. Z., Derjagina O. G., Tomashov N. D.: Croat. Chim. Acta *44*, 7 (1972).
10. Armstrong R. D., Firman R. E.: J. Electroanal. Chem. *34*, 391 (1972).

Translated by K. Micka.