

Impedance of molybdenum electrodes in a soda-lime-silica glass melt

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Impedance measurements at molybdenum electrodes in a soda-lime-silica glass melt were carried out in a frequency range of 0.1 to 10^5 Hz. The spectra obtained were quite different depending on the DC potential superimposed. Thus, spectra obtained from anodically passivated electrodes could be clearly distinguished from those of electrodes with a MoSi_x -surface layer and from unprotected electrodes. Although the physical interpretation of the spectra obtained is very difficult, and up to now unsatisfactory, impedance measurements seem to be suitable for measuring and controlling passivating layers at molybdenum electrodes.

Impedanz von Molybdänelektroden in einer Kalk-Natronsilicatglasschmelze

Impedanzmessungen an Molybdänelektroden in einer Kalk-Natronsilicatglasschmelze wurden in einem Frequenzbereich von 0,1 bis 10^5 Hz durchgeführt. Abhängig vom überlagerten Gleichspannungspotential wurden sehr unterschiedliche Spektren erhalten. Impedanzspektren anodisch passivierter Elektroden unterschieden sich klar von solchen, die an Elektroden mit einer MoSi_x -Deckschicht oder an ungeschützten Elektroden aufgenommen wurden. Obwohl die physikalische Interpretation der Impedanzspektren sehr schwierig und bisher nicht in befriedigender Weise gelungen ist, scheinen Impedanzmessungen geeignet zu sein, passivierende Schichten auf Molybdänelektroden zu messen und zu kontrollieren.

1. Introduction

Electric melting of glass is a technique with increasing importance for industrial applications. Today, molybdenum is the most commonly used electrode material. The most important problem associated with this material is the heavy corrosion in some glass melts. Over the last few years, efforts have been made to minimize the corrosion rate. One of these techniques is to superimpose a small DC potential on the AC-heating voltage [1]. In this technique, the molybdenum electrodes are usually set on an anodic potential ("anodic passivation"). Another technique is the "low-frequency passivation", first developed in Czechoslovakia [2]. Here, the applied heating current has a frequency of 6 to 12 Hz. Both techniques have already been applied to lead glass melts in Czechoslovakian industry.

The anodic passivation technique is especially successful in achieving a drastic decrease in the corrosion rate. The prerequisite, however, is an accurate "modelling" of the electrode configuration in order to obtain comparable DC potentials and passivation effects at all electrodes. During melting, the electrode geometry changes with time, due to corrosion and electrode renewal. This also leads to changes in passivation effects and, in many cases, to an increase in the corrosion rate.

Electrochemical measurements are quite suitable for investigating the corrosion behaviour of molyb-

denum electrodes in contact with glass melts [3 to 5]. With the aid of impedance measurements it should be possible to distinguish active and passive states of molybdenum electrodes.

2. Experimental

All experiments were carried out in a soda-lime-silica glass melt with the basic composition (in mol%) of 74 SiO_2 , 16 Na_2O and 10 CaO . The premelted glass was placed in an alumina crucible, located in a large alumina muffle tube inside a SiC resistance-heated furnace. Molybdenum rods (5 mm in diameter) embedded in small alumina tubes were used as working electrodes; the counter electrode was a platinum plate with an area of approximately 2 cm^2 ; the reference electrode was a zirconia/air probe, in principle already described in [6].

A commercially available impedance apparatus (Im5d, Zahner, Kronach (FRG)) was used. Its main component is the potentiostat, which was connected to a microcomputer via digital/analog and analog/digital converters. The frequency was varied over a wide range between 10^{-1} and 10^5 Hz. Measurements at frequencies $< 10^{-1}$ Hz, although theoretically possible with the aid of the equipment used, were not carried out since they are very time-consuming and the molybdenum electrode may have changed its characteristics during measurements. Measurements at frequencies $> 10^5$ Hz cannot provide any information about the molybdenum electrode, because

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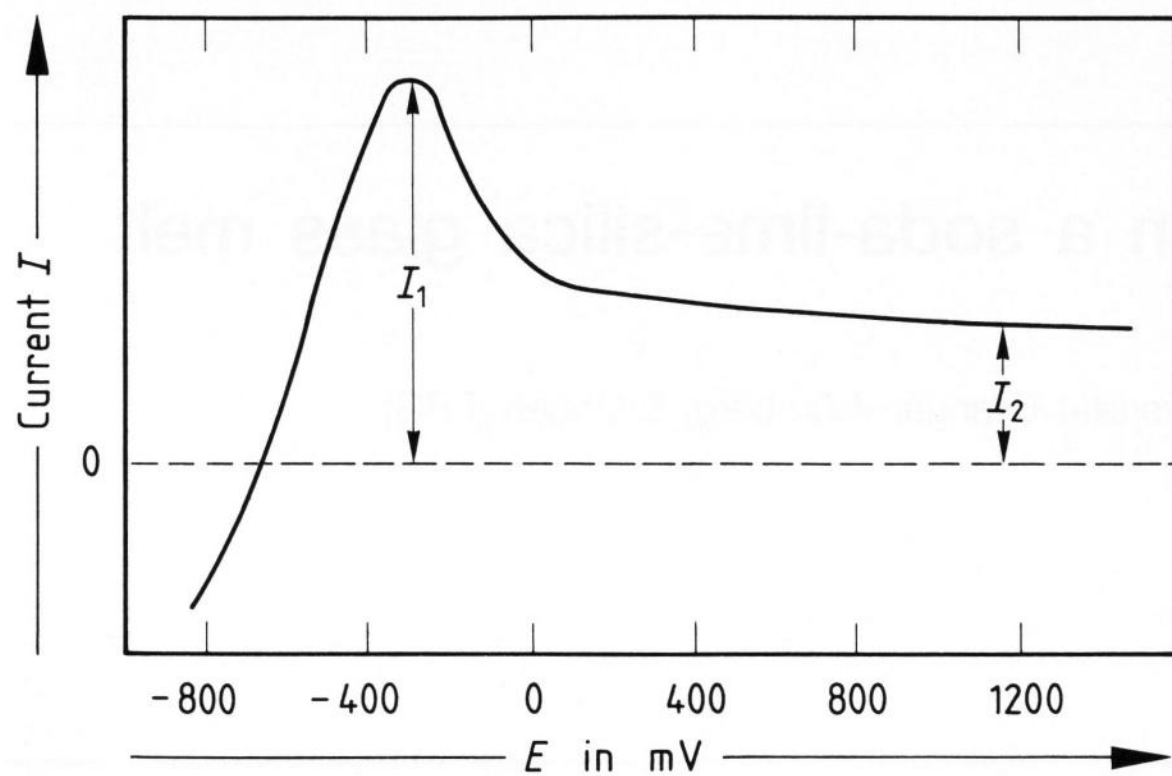


Figure 1. Current-potential curve recorded at a molybdenum electrode in a soda-lime-silica glass melt. $\vartheta = 1200\text{ }^{\circ}\text{C}$, scan rate = 1 mV/s , I_1 = maximum current at -300 mV , I_2 = constant current at 500 mV .

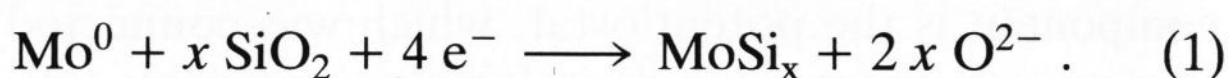
they are severely affected by the inductance of connecting wires.

The alternating potential had an amplitude of 10 mV , and a DC potential in the range of -1000 to $+1000\text{ mV}$ was superimposed on it. All impedance spectra were recorded automatically, and were represented graphically on $\lg |\text{impedance}|$ versus $\lg (\text{frequency})$ and $|\text{phase angle}|$ versus $\lg (\text{frequency})$ plots. The uncertainty in the phase angle, φ , is about 0.3° . In some cases, an equivalent circuit was suggested and the impedance spectra were simulated numerically.

The current-potential curves were measured using the same electrode configuration, the electronic equipment was a potentiostat (POS 73, Bank Elektronik, Göttingen (FRG)) with a linear scan generator. The current-potential curves were recorded using a scan rate of 1 mV/s .

3. Results and discussion

Figure 1 shows a current-potential curve, recorded at a molybdenum electrode in a soda-lime-silica glass melt using a scan rate of 1 mV/s and at a temperature of $1200\text{ }^{\circ}\text{C}$. At the starting potential of -700 mV , a negative current can be seen. As already described in [5], this is due to the reduction of the silicate melt and the formation of molybdenum silicide at the electrode surface (equation (1)),



When the potential is increased, the current increases very rapidly, reaching a maximum (I_1) at about -300 mV ; at larger potentials, the current decreases again and reaches an almost constant value (I_2) at about $+500\text{ mV}$. Positive currents indicate that molybdenum is oxidized:

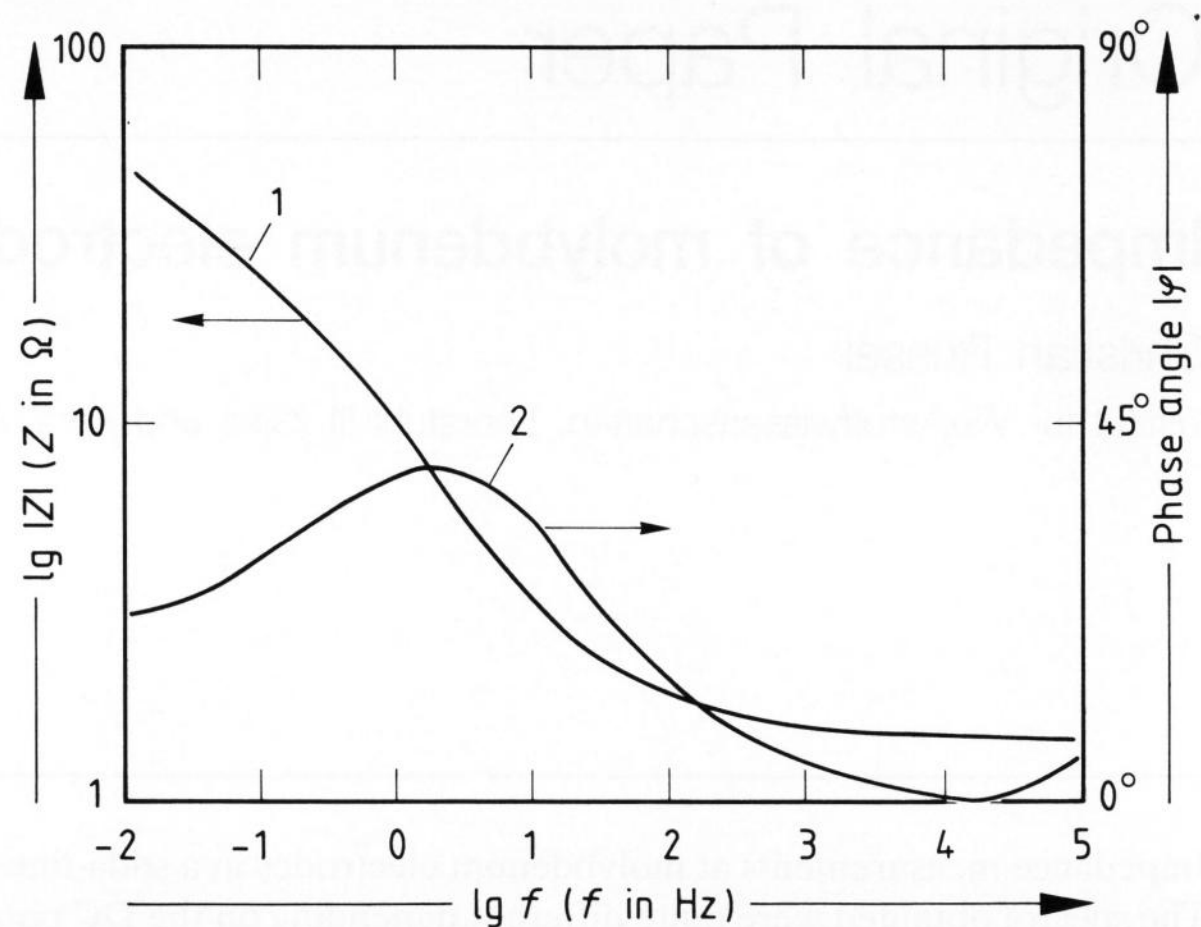
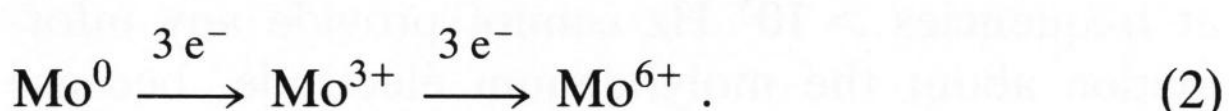


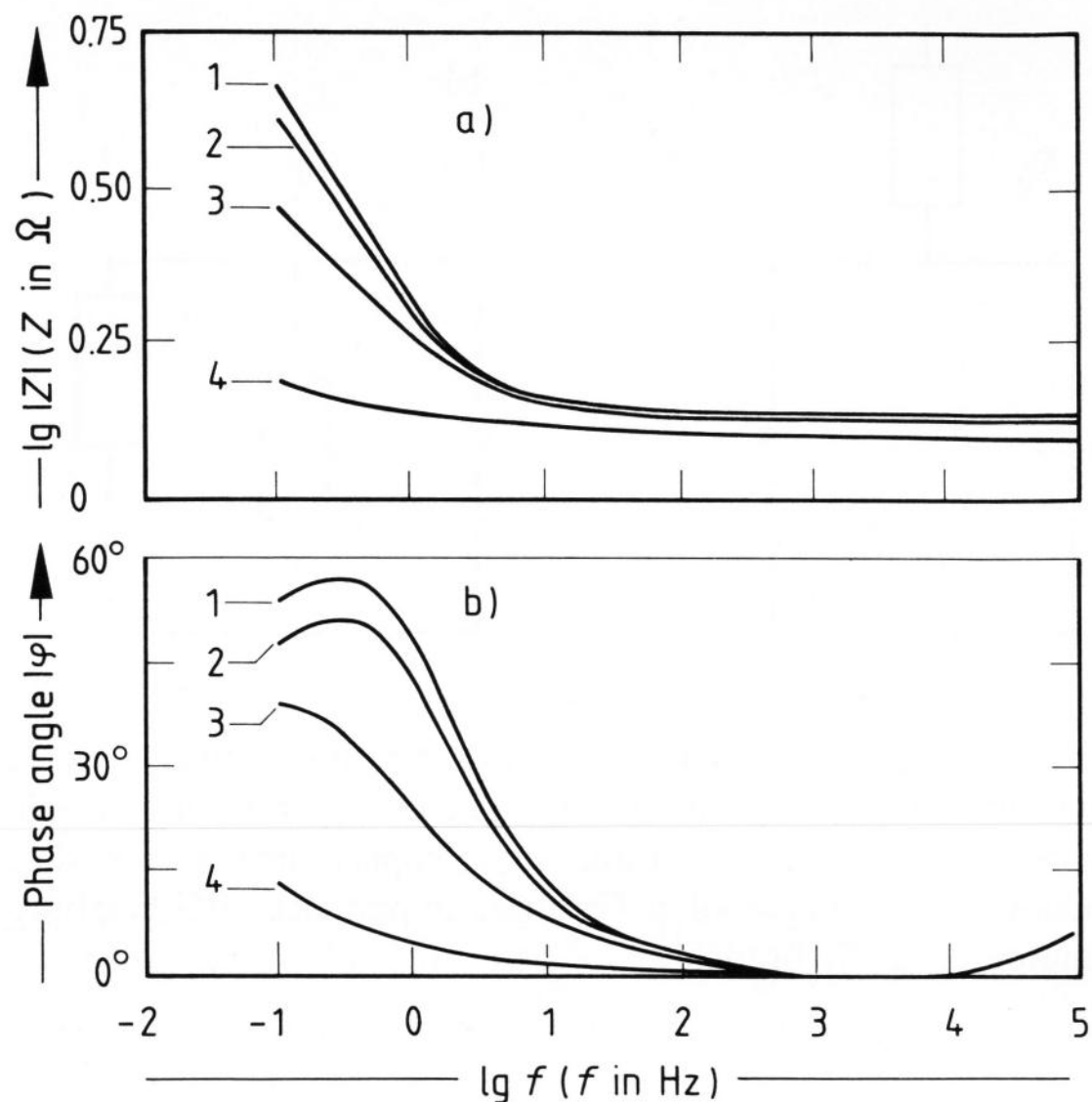
Figure 2. Spectra of impedance and phase angle of a molybdenum electrode in a soda-lime-silica glass melt. $\vartheta = 1200\text{ }^{\circ}\text{C}$, superimposed DC potential = -1000 mV . Curve 1: impedance $|Z|$, curve 2: phase angle $|\varphi|$.

At the maximum in the current-potential curve (figure 1), the corrosion rate is a maximum. The decrease of the current is due to the formation of a protective layer with a high molybdenum oxide content at the electrode surface, which hinders further dissolution of the electrode. If anodic protection of the electrode is required, a DC potential $> 400\text{ mV}$ should be superimposed on the heating current.

Figure 2 shows an impedance spectrum recorded at a molybdenum electrode in a soda-lime-silica glass melt at $1200\text{ }^{\circ}\text{C}$. The frequency range was 10^{-2} to 10^5 Hz and the DC potential superimposed was -1000 mV . At 10^{-2} Hz , $|Z|$ possessed a value of about $30\text{ }\Omega$, decreased with increasing frequency up to 10^4 Hz and then reached a constant value of about $1.5\text{ }\Omega$. The phase angle at a frequency of 10^{-2} Hz was about -20° , decreased down to a value of -40° at a frequency of about 2 Hz and then increased again. At a frequency of about $3 \cdot 10^4\text{ Hz}$, a phase angle of 0° was reached and became positive at further increasing frequencies due to the inductance of the connecting wires.

Figures 3a and b show the impedance and phase angle spectra recorded at $1200\text{ }^{\circ}\text{C}$ in a frequency range of 10^{-1} to 10^5 Hz at superimposed DC potentials of -200 , -400 , -600 and -800 mV (curves 1 to 4). The impedance spectra were recorded in one series of experiments. The potential first applied to the molybdenum electrode was -200 mV ; after each measurement was completed, the potential was further decreased and, after waiting 30 min , a new impedance spectrum was recorded.

Curve 1 in figure 3b was recorded at a superimposed DC potential of -200 mV . The phase angle φ was negative at lower frequencies, reached a value of 0° at about $3 \cdot 10^3\text{ Hz}$, then changed its sign and became positive at further increasing frequencies due to inductive effects. $|\varphi|$ possessed a well-pronounced

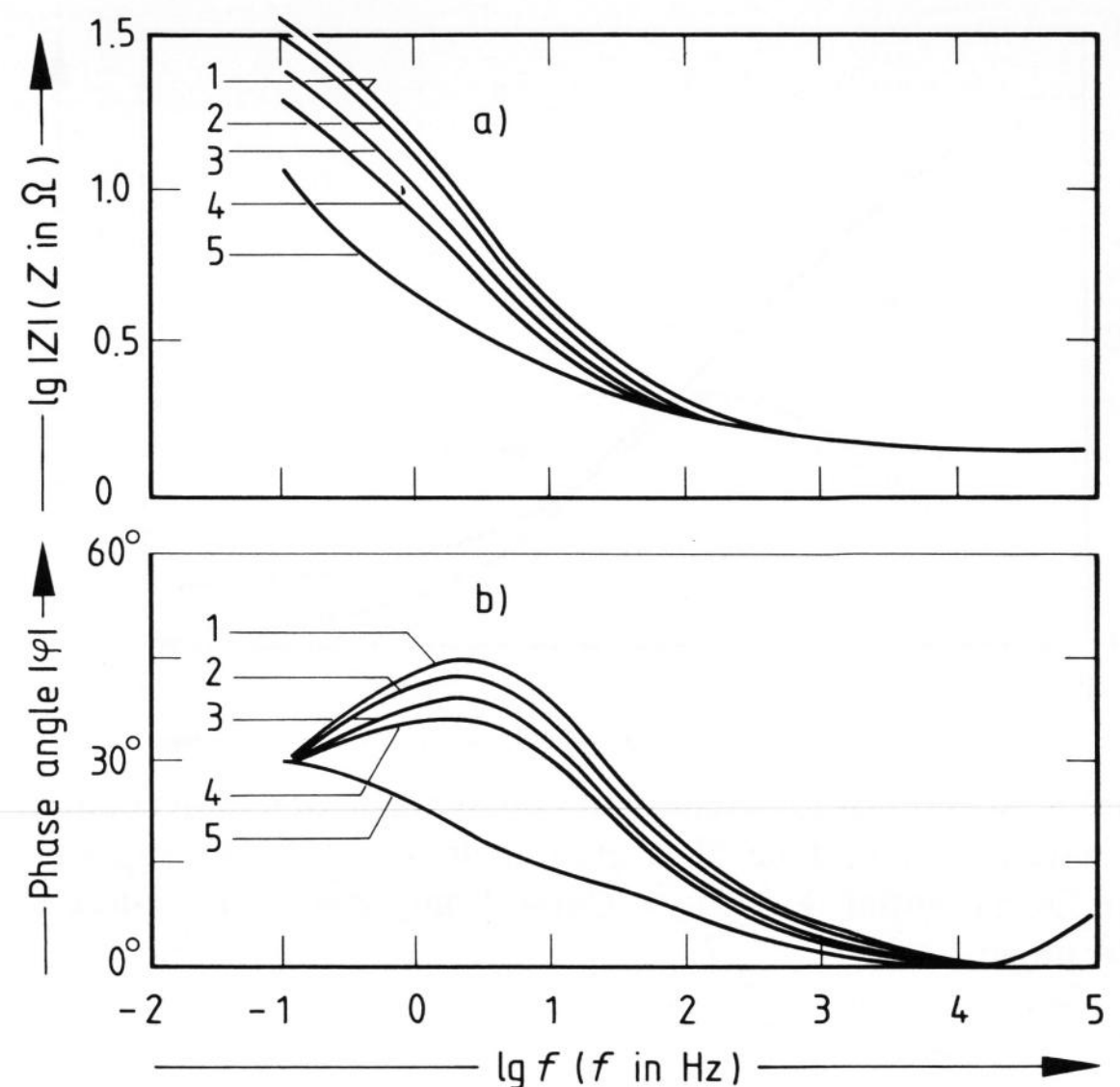


Figures 3a and b. Spectra of impedance (figure a) and phase angle (figure b) of a molybdenum electrode in a soda-lime-silica glass melt. $\vartheta = 1200\text{ }^{\circ}\text{C}$, superimposed DC potentials: curve 1 = -200 mV , curve 2 = -400 mV , curve 3 = -600 mV , curve 4 = -800 mV .

maximum ($\varphi \approx -58^{\circ}$) at about 0.6 Hz , at further increasing frequencies, $|\varphi|$ decreased again. Curve 2 was recorded at a superimposed DC potential of -400 mV . The curve obtained was quite similar to curve 1, the maximum in $|\varphi|$ was reached at the same frequency but the related phase angle was slightly higher ($\varphi \approx -50^{\circ}$). According to figure 1, superimposed DC potentials of -200 and -400 mV lead to high corrosion rates because the current-potential curve has its maximum in this potential range and, therefore, the molybdenum electrode is in an active state. Curve 3 was recorded at a superimposed DC potential of -600 mV . Here, no maximum can be seen in the $|\varphi|$ versus $\lg(\text{frequency})$ plot. At a frequency of 0.1 Hz , the phase angle has a value of about -39° . At further decreasing DC potential (-800 mV), $|\varphi|$ has a value of only 12° at a frequency of 10^{-1} Hz . The curves 2 and 3 were recorded in a potential region (-600 and -800 mV), at which the glass melt is reduced and molybdenum silicide is formed at the electrode (figure 1).

In the $\lg |Z|$ versus $\lg(\text{frequency})$ plot (figure 3a), fairly similar behaviour can be seen. In all cases, the impedance decreases with increasing frequency. But the values of $|Z|$ at a frequency of 0.1 Hz were considerably different: the higher the superimposed DC potential, the higher the value of $|Z|$. For curve 4 in figure 3a, $|Z|$ depended only very slightly on the frequency.

Thus, as shown in figure 3a, impedance measurements can be used to distinguish between an active state of the molybdenum electrode (related to a high corrosion rate), and a state in which molybdenum silicide is formed. In figures 3a and b, curves 3 and 4



Figures 4a and b. Spectra of impedance (figure a) and phase angle (figure b) of a molybdenum electrode in a soda-lime-silica glass melt. $\vartheta = 1200\text{ }^{\circ}\text{C}$, superimposed DC potential: -1000 mV . Curve 1: recorded immediately after applying the potential, curve 2: after 5 min, curve 3: after 10 min, curve 4: after 15 min, curve 5: after 30 min.

were recorded in a series of experiments applying each potential 30 min before measurement. But by comparison with figure 2, it can be assumed that the impedance spectra are influenced not only by the DC potentials superimposed, but also by the length of time for which they are applied.

Further experiments were made in order to clarify time-dependent effects. A potential of -1000 mV was applied to the electrode and, immediately afterwards, another series of impedance spectra were recorded (figure 4a). As shown in figure 4b $|\varphi|$ of the first spectrum (curve 1) showed a fairly well-pronounced maximum at a frequency of around 2 Hz . Spectra recorded after 5, 10 and 15 min are shown in figures 4a and b as curves 2, 3, and 4, respectively. The maximum is increasingly less well-pronounced with increasing duration of the potential being applied. Curve 5 was recorded 30 min after applying the potential to the molybdenum electrode. Here, a maximum cannot be seen and the whole curve approaches to those of figures 3a and b, curve 4. Fairly similar behaviour can also be seen in the plot $\lg |Z|$ versus $\lg(\text{frequency})$.

Figure 5 shows an impedance spectrum recorded after a superimposed DC potential of $+800\text{ mV}$ was applied to the molybdenum electrode for 30 min. This potential corresponds to the passive region of figure 1. The $|\varphi|$ spectrum possesses a well-pronounced maximum of $|\varphi|$ ($\varphi \approx -36^{\circ}$) at a frequency of about 6 Hz . At higher frequencies $|\varphi|$ decreases and becomes zero at a frequency of about $8 \cdot 10^4\text{ Hz}$. At a frequency of 0.1 Hz , $|\varphi|$ decreases to a value of about 15° and $|Z|$ to a value of about $60\text{ }\Omega$. The high values of $|Z|$ at low frequencies indicate the

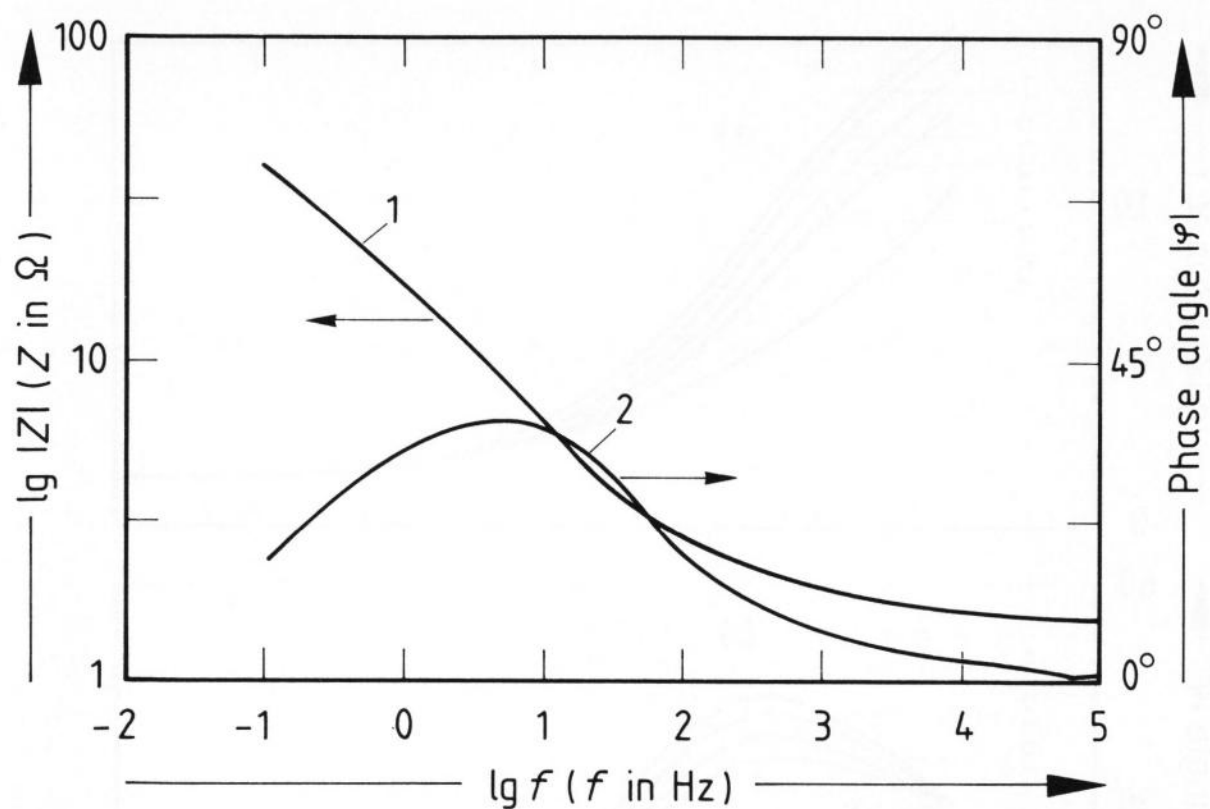
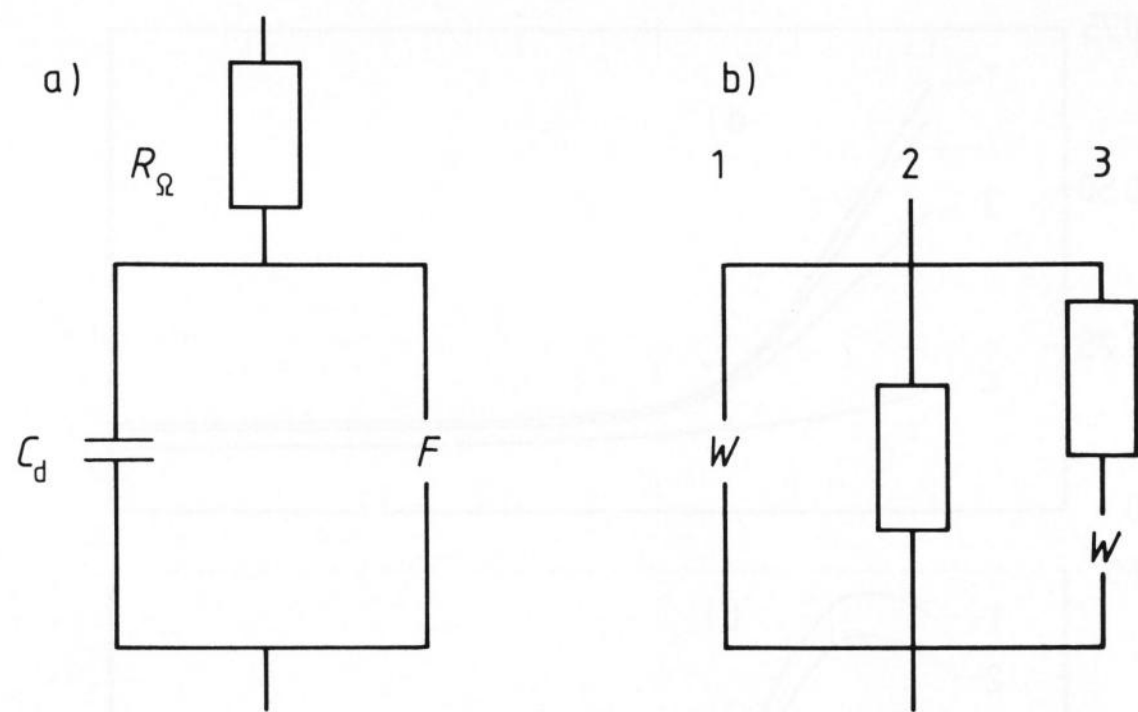


Figure 5. Spectra of impedance and phase angle of a molybdenum electrode in a soda-lime-silica glass melt. $\vartheta = 1200\text{ }^{\circ}\text{C}$, superimposed DC potential: + 800 mV. Curve 1: impedance $|Z|$, curve 2: phase angle $|\varphi|$.

formation of a layer with high Ohmic resistance at the electrode surface. It already has been shown by SEM and EDX in [5] that, in this potential region, a diffuse interface with high molybdenum oxide content is formed at the electrode.

Although the impedance spectra of figure 3a, curves 1 and 2, are fairly similar to that of figure 5, the curves clearly can be distinguished: the frequencies of the $|\varphi|$ maxima are quite different. At a DC potential of -200 or -400 mV, the maximum is observed at a frequency of 0.6 Hz, while at a DC potential of + 800 mV, it is observed at a frequency of 6 Hz.

The physical interpretation of the impedance spectra obtained are very complicated. In principle, however, equivalent circuits can be suggested and the spectra numerically simulated. Generally all impedance spectra at electrodes follow the equivalent circuit given by figure 6a. The capacitance C_d is related to the electrochemical double layer of the electrode/melt interface, while the resistor R_Ω takes the place of the Ohmic resistance of the melt. The Faradaic impedance F describes all other processes at the electrode, such as the electron transfer itself, adsorption and desorption processes at the electrode surface, diffusion processes in the melt, the formation of any layers, diffusion processes within these layers and capacitive effects caused by these layers. At the most DC potentials superimposed, layers or interfaces are formed at the electrode. Thus, the Faradaic impedance has to be described by a fairly complex system. Indeed, the spectra of figures 2 to 5 cannot be simulated with sufficient precision, by simple equivalent circuits. Figure 6b shows a more complex Faradaic impedance which enables the simulation of impedance spectra of figure 2 with sufficient precision, i.e. with a maximum deviation of the phase angle within the limits of error ($\Delta\varphi < 0.3^\circ$). It should be noted that if any element of the equivalent circuit is omitted, the experimental curve cannot be simu-



Figures 6a and b. Circuit diagrams for impedance spectra simulation, a) equivalent circuit for impedance spectra. R_Ω : Ohmic resistance of the melt, C_d : double layer capacitance, F : Faradaic impedance; b) example of a Faradaic impedance. W : Warburg parameter, 1, 2, 3: branches.

lated with a maximum deviation of the phase angle below 1° . Although intensively investigated, no other equivalent circuit was found which could describe the experimental curve with sufficient precision. The appearance of Warburg parameters, W [7 and 8], in the equivalent circuit proves that diffusion processes play an important part in the electrode reaction. A possible physical interpretation of the equivalent circuit is as follows:

- branch 1 accords to a diffusion-controlled reaction,
- branch 2 to a kinetically hindered electron transfer,
- branch 3 to a quasireversible electron transfer (kinetically hindered electron transfer influenced by diffusion).

Kinetically hindered electron transfer reactions at a superimposed DC potential of -1000 mV easily can be explained by the electrode reaction itself (equation (1)): SiO_2 is reduced to elementary silicon. Thus, extensive structural changes are necessary. According to the theory of electron transfer, these reactions possess high activation free enthalpies, due to high "inner reorganization" energies [9 and 10].

As already mentioned, the physical interpretation of the impedance spectra is very complicated and the suggestions made are preliminary.

4. Conclusions

At different DC potentials applied to molybdenum electrodes, quite different impedance spectra were obtained. Although physically not fully understood, impedance measurements could be used to measure and control passivating layers at molybdenum electrodes. In technical glass melts, this could facilitate the proper superposition of DC potentials in order to obtain anodically passivated molybdenum electrodes and thus minimize the corrosion rate.

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