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# On the Warburg Parameter of the Ag/AgI Electrode

*K. Kvastek and V. Horvat*

*Center for Marine Research and Department of Physical Chemistry, »Ruđer Bošković« Institute, 41001 Zagreb, P.O.B. 1016, Croatia, Yugoslavia*

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The possible origins of frequent deviations from the calculated and experimentally obtained values of the Warburg parameter of the Ag/AgI electrode are discussed. Following the considerations of possible conditions for classical Warburg impedance to appear in solid AgI, it is suggested that the overall Warburg impedance of the Ag/AgI electrode could be considered as the sum of the Warburg impedances in series, one in the solid, and the other in the solution phase. In addition, the influence of diffusion controlled adsorption of $I^-$ ions in parallel with diffusion controlled ion-transfer on the experimentally obtained values of the Warburg parameter is discussed.

A different theoretical approach to the analysis of the Warburg impedance of the Ag/AgI electrode is suggested, different from those formerly applied.

## INTRODUCTION

The identification and characterization of the processes responsible for the impedance of the Ag/AgI electrode were subjects of a number of papers.[1-10] In order to carry out a meaningful analysis of the impedance data, all authors suggested an analytical model of the system, and most of them expressed it in the form of an equivalent circuit. Some authors[1,3,4] treated the Ag/AgI electrode as completely polarizable, i. e. like a series connection of double-layer capacitance and AgI and electrolyte solution resistances. The classical Randles'circuit, which implies the simultaneous activation and diffusion controlled interphasial ion transfer, i. e. double-layer capacitance in parallel with a series connection of ion transfer resistance and Warburg impedance, was employed by Barshatky.[2] Peverelli and van Leeuwen[5,6] suggested two classical Randles'circuits in series, where one Randles'circuit pertains to the solid Ag/AgI interphase, while the other to the AgI/solution interphase. Later on, a completely activation controlled interphasial ion transfer, i. e. double-layer capacitance in parallel with ion transfer resistance, was suggested by van Leeuwen and co-workers,[7] while in their recent paper[8] a completely diffusion controlled interphasial ion transfer, i. e. double-layer capacitance and Warburg impedance in parallel, was proposed. Finally, the present authors[9,10] proposed a diffusion controlled interphasial ion transfer coupled with reactant adsorption process, i. e. an equivalent circuit characterized by parallel connection of high frequency double-layer capacitance, adsorption impedance and Warburg impedance. All the authors, however, discussed the theory underlying the use of the chosen circuits, but all of them obtained discrepancies between the theory and the experiment. Several reasons were given for the dissapointing results: The surface roughness effect,[1-6,9,10] instrumental shortcomings[6] and the influence of the characteristics of the solid AgI.[5,6,9,10]

The purpose of the present paper is to elaborate in more detail the factors contributing to the observed deviations. The emphasis is put on the significant differences between the predicted and the observed values of the Warburg parameter which determines the Warburg impedance, one of the main regions of usual electrolytic interest. The deviations have commonly been observed by all authors who employed the Warburg impedance sequence, regardless of the choice of the equivalent circuit.[2,5,6,8-10] A discussion is presented to give a physical insight into some of the processes which could contribute to the observed anomalies.

## EXPERIMENTAL

A small amplitude (± 5 mV) sinusoidal voltage as an input signal is put on the electrolytic cell consisting of the Ag/AgI spherical microelectrode set at the centre of the large Pt-cylindrical counter electrode. Impedance measurements are performed at equilibrium Ag/AgI electrode potentials, due to the corresponding concentrations of $I^-$ and $Ag^+$ ions in 0.01 mol $dm^{-3}$ $KNO_3$ as the supporting electrolyte, at 298 K. From the response signal, the cell impedances are measured directly, in the series capacitance and resistance mode in 20 Hz—20 kHz frequency domain where impedance is defined. More details of impedance measurements are given elsewhere.[9]

The Ag/AgI electrodes are electrolitically prepared from 0.01 mol $dm^{-3}$ NaI as the electrolyte. The marks of electrodes, operating conditions for electrolysis and calculated thicknesses of AgI-layers are given in Table I.

TABLE I

*Marks of Electrodes, Operating Conditions for Preparation of Ag/AgI Electrodes and Calculated Thicknesses of the AgI-Layers*

| Mark of electrode | Apparent area of electrode<br>$cm^2$ | Current density<br>$mA/cm^2$ | Thickness of AgI-layer<br>$10^{-4}$ cm |
|---|---|---|---|
| 1 | 0.0304 | 0.16 | 0.844 |
| 2 | 0.0379 | 0.16 | 0.856 |
| 3 | 0.0472 | 0.42 | 2.090 |
| 4a | 0.0244 | 1.00 | 1.027 |
| 4b | 0.0244 | 1.00 | 2.311 |
| 4c | 0.0244 | 1.00 | 3.595 |
| 4d | 0.0244 | 1.00 | 4.879 |

## THEORETICAL RESULTS

The theory of electrode kinetics in liquid electrolytes takes into consideration the effect of diffusion of the species participating in an electrode reaction, toward and away from an electrode. The diffusion polarization leads to an impedance, usually referred to as Warburg diffusion impedance.[11-13] The unit area Warburg impedance for a single reaction at a single working electrode was originally derived for the usual electrochemical case of electroneutrality arising from the presence of the supporting, indifferent electrolyte. In the simplest case of semi-infinite linear diffusion, the Warburg impedance, $Z_W$, is given by:

$$Z_W = (1 - j)\, \sigma \omega^{-1/2} \tag{1}$$

where $\omega$ is the angular frequency, $j$ is the imaginary unit, while $\sigma$ is the so called Warburg parameter. The usual expression for $\sigma$, applied to a single working electrode where oxidized and reduced species (diffusion coefficients $D_o$, $D_r$ and concentrations $C_o$, $C_r$) are present at the electrode, may be written at the equilibrium electrode potential as:

$$\sigma = (RT/n^2 F^2 2^{1/2})\, (1/C_o D_o^{1/2} + 1/C_r D_r^{1/2}) \tag{2}$$

Here, $n$ is the number of electrons participating in an electrode reaction, while the other symbols have their usual meaning.

For the case of a metal-ion/metal electrode, where $C_r$ is invariable by definition, eqn. (2) leads to a simpler equation:

$$\sigma = RT/n^2 F^2 C_o (2D_o)^{1/2} \tag{3}$$

Eqn. (3) applied to the Ag/AgI, $I^-$ ($Ag^+$) electrode at 298 K and $D_{I^-} = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $D_{Ag^+} = 1.4 \times 10^{-5}$ cm$^2$ s$^{-1}$ gives the commonly used equation:[1,5,6,8-10]

$$\sigma_{I^-} = 4.2 \times 10^{pI-2} \tag{4a}$$

$$\sigma_{Ag^+} = 5.0 \times 10^{pAg-2} \tag{4b}$$

In the case of the Ag/AgI electrode, both ions are simultaneously present in the electrolyte solution due to the solubility product of AgI. Therefore, the overall Warburg impedance is the parallel combination of both mass transfer polarizations. Consequently, the reciprocal value of the overall $\sigma$ value is the sum of reciprocal values of $\sigma_{I^-}$ and $\sigma_{Ag^+}$. However, the coupling becomes evident only in the restricted pI and pAg range, $pI > 7$ and $pAg > 7$, where both ions are present in almost the same concentrations.

## EXPERIMENTAL RESULTS

Some typical results of the Ag/AgI electrode impedance $Z = Z' - jZ''$, obtained after subtraction of the ohmic resistance, are given in Figures 1 and 2. In Figure 1 the complex impedance plane representation is given for the Ag/AgI electrode 2, at several pI and pAg values. In Figure 2 the same presentation is drawn for Ag/AgI electrodes 4a and 4b at two different pI values. Details of the electrode preparation are given in Table I.

The straight line segments obtained in Figures 1 and 2 indicate Warburg behaviour of the electrode impedance, although phase angles greater than $\pi/4$ indicate an additional capacitive behaviour, being more pronounced as pI and pAg increase. The complete behaviour of the Ag/AgI electrode impedance was discussed previously[9,10], where it was stated that the impedance data could be analyzed according to the equivalent circuit for the reversible electrode reaction with reversible reactant adsorption. In that case the values of the Warburg parameter could be obtained as reciprocal intercepts of $Y'/\omega^{1/2}$ vs. $\omega$ linear dependences[13] where $Y'$ denotes the real part of the electrode admittance.

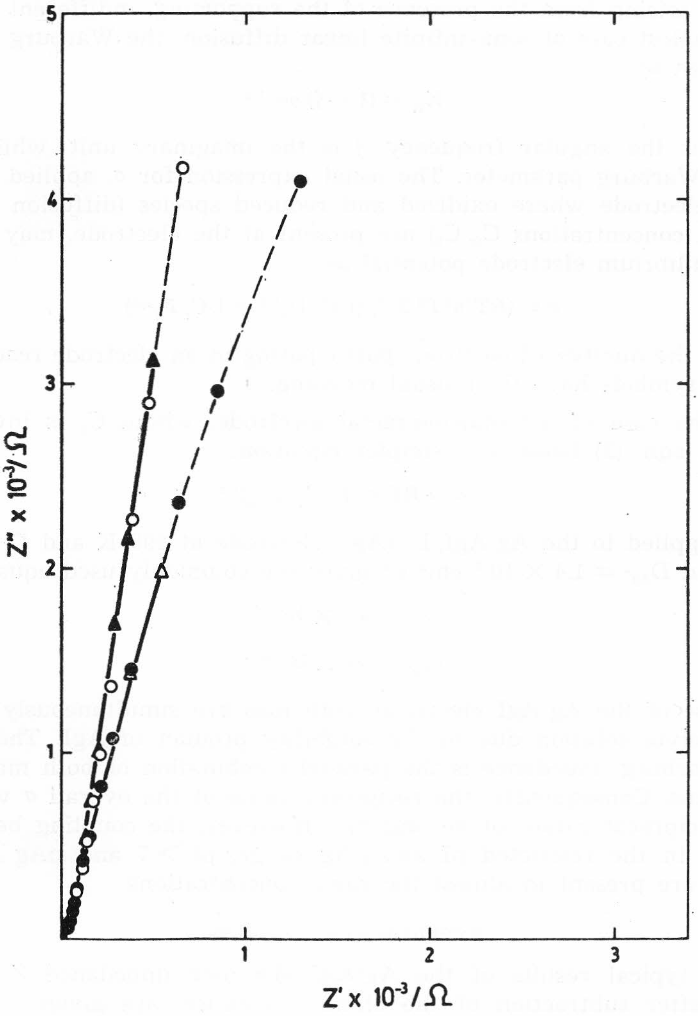

Figure 1. Complex impedance plane for the Ag/AgI electrode 2 in 0.01 mol dm$^{-3}$ KNO$_3$ and: (— — —) (○) pI = 6.4; (●) pI = 3.9; (———) (▲) pAg = 6.5; (△) pAg = 4.9.

Thus obtained $\sigma$ values for several Ag/AgI electrodes are in dependence on pI and pAg given in Figure 3, while the same dependence of $\sigma$ values obtained for the single Ag/AgI electrode of various thicknesses of the AgI-layer is given in Figure 4. For details see Table I.

Note that all $\sigma$ values drawn in Figures 3 and 4 are normalized to the geometrical or apparent electrode area, which leaves the influence of the microsurface area, if relevant, to be further investigated.

From Figures 3 and 4, taken together, it appears that log of $\sigma$ values are not linear functions of pI and pAg. At low pI, $\sigma$ values are anomalously high, while at high pI and pAg, $\sigma$ values are much lower then it is predicted by eqn. (4), the latter result is drawn by thin lines in Figures 3 and 4. Fairly good agreement is obtained only at lower pAg, if at pAg = 5 reasonable surface roughness factors are taken into account. Here it must be pointed out that $\sigma$ values multiplied by the corresponding surface roughness factor in the whole pI and pAg range investigated, would not much improve results, particularly in the low pI range where it would give a much more pronounced anomalous behaviour of $\sigma$ values. It is evident from Figures 5 and 6, where $\sigma$ values, normalized to the apparent electrode area and corrected for surface roughness factor, are given in dependence on pI and pAg.

From data in Figures 3—6 it can be concluded that the operating conditions for the preparation of Ag/AgI electrodes, as well as the thickness of the AgI-layer, have significant consequences for the magnitudes of $\sigma$ values if normalized to the apparent electrode area. This effect could be completely

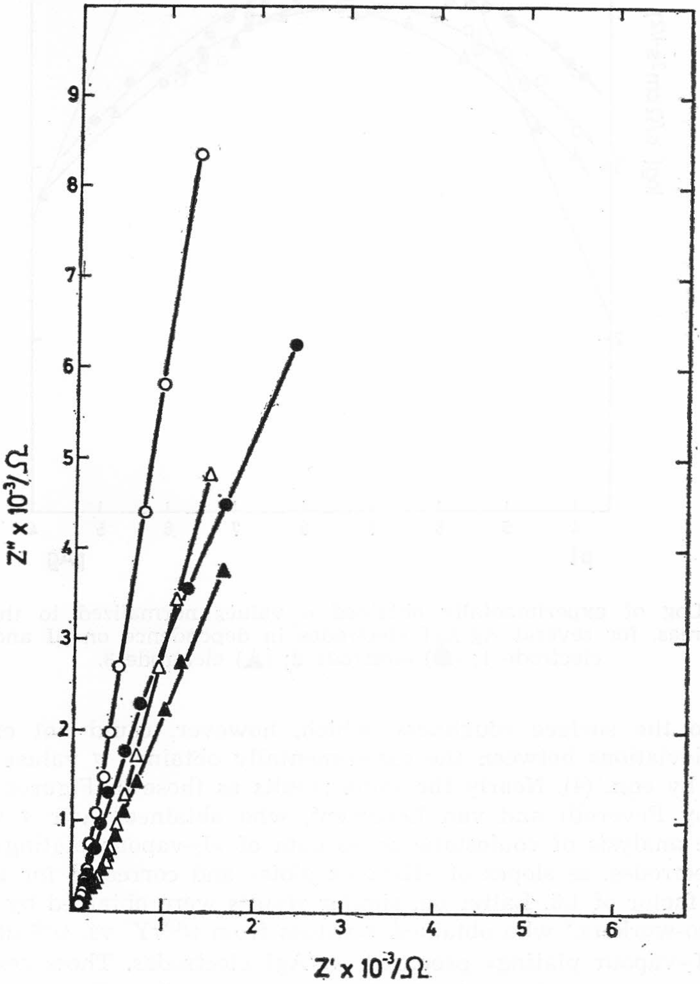

Figure 2. Complex impedance plane for the Ag/AgI electrode 4 in 0.01 mol dm$^{-3}$ KNO$_3$: (○) electrode 4a, pI = 7,0; (●) electrode 4a, pI = 3.0; (△) electrode 4b, pI = = 7.9; (▲) electrode 4b, pI = 2.9.

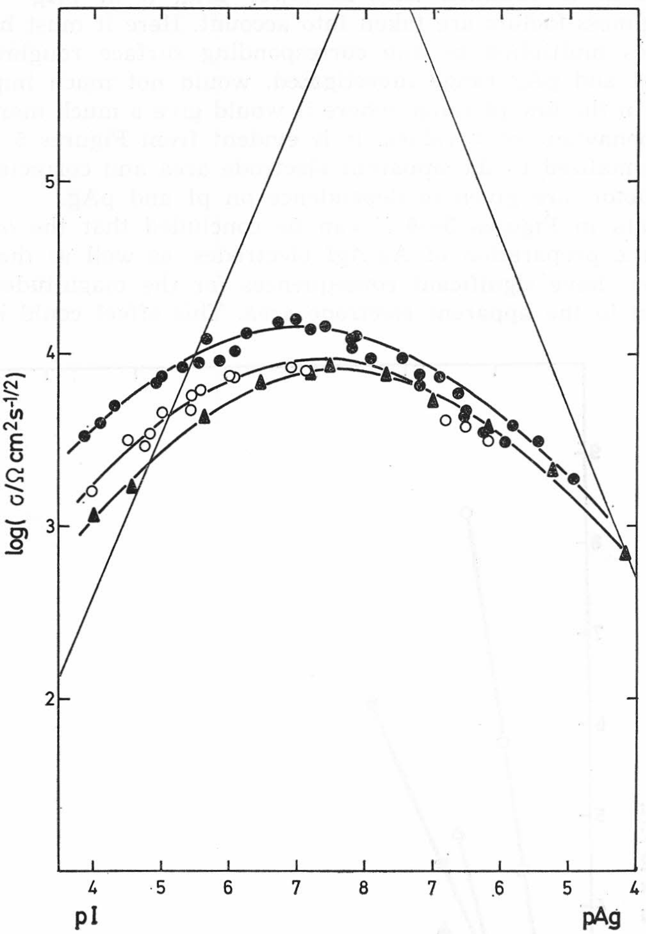

Figure 3. Log of experimentally obtained $\sigma$ values normalized to the apparent electrode areas, for several Ag/AgI electrodes in dependence on pI and pAg: (○) electrode 1; (●) electrode 2; (▲) electrode 3.

ascribed to the surface roughness, which, however, could not explain the observed deviations between the experimentally obtained $\sigma$ values and those calculated by eqn. (4). Nearly the same results as those in Figures 3—6 were obtained by Peverelli and van Leeuwen[6], who obtained their $\sigma$ values following the analysis of coulostatic pulse data of »$I_2$-vapour plating« prepared Ag/AgI electrodes, as slopes of »Randles plots« and corrected for the surface roughness factor of 1.5. Latter on, similar results were obtained by van Leeuwen and co-workers,[8] who obtained $\sigma$ values from $\omega^{1/2}/Y'$ vs. $\omega^{1/2}$ dependences for flat, »$I_2$-vapour plating« prepared Ag/AgI electrodes. These results, together with ours reported previously[9,10], are summarized in Figure 7. Note that data from refs.[6] and [8] are estimated from graphical representations, and therefore are not quite accurate.

The data in Figure 7, together with those in Figures 3—6, clearly show nearly the same behaviour of $\sigma$ values, regardless of the following parameters:

(i) different methods of impedance measurements,
(ii) different methods of impedance data analysis,
(iii) different methods of preparation of Ag/AgI electrodes,
(iv) different surface roughness factors.

Consequently, all of these parameters can be immediately eliminated as possible sources of the observed discrepancies. Therefore, it can be concluded, that the observed deviations of $\sigma$ values are due to some characteristics, inherent to the investigated system, which are not accounted for in the theoretical approach given by eqn. (4).

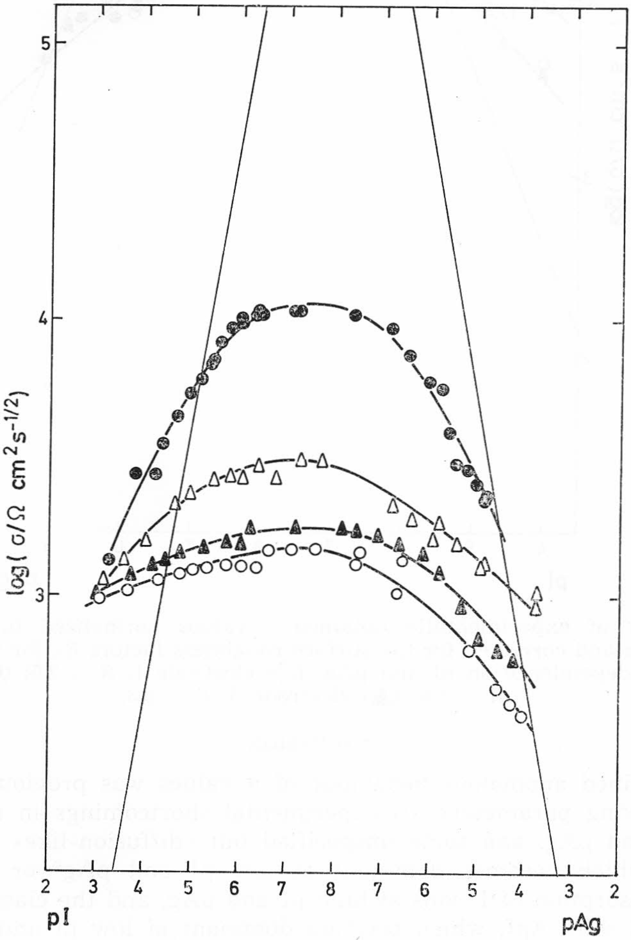

Figure 4. Log of experimentally obtained $\sigma$ values normalized to the apparent electrode area, for the Ag/AgI electrode of various thicknesses of the AgI-layer, in dependence on pI and pAg: (●) electrode 4a; (△) electrode 4b, (▲) electrode 4c; (○) electrode 4d.

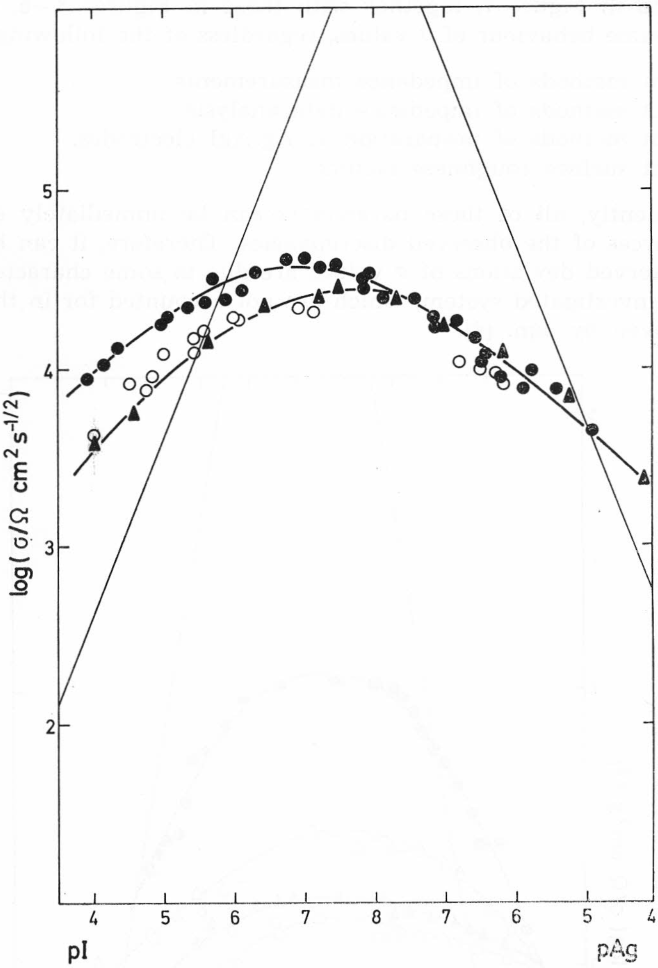

Figure 5. Log of experimentally obtained $\sigma$ values normalized to the apparent electrode areas and corrected for the surface roughness factors $R_f$, for several Ag/AgI electrodes, in dependence on pI and pAg: (○) electrode 1, $R_f = 2.6$; (●) electrode 2, $R_f = 2.6$; (▲) electrode 3, $R_f = 3.3$.

## DISCUSSION

The obtained anomalous behaviour of $\sigma$ values was previously explained by the following parameters: (i) experimental shortcomings in measurements at high pI and pAg, and some unspecified but »diffusion-like« impedance in solid AgI, which becomes dominant at low pI and pAg[6] or (ii) influence of specific adsorption of $I^-$ ions at high pI and pAg, and the classical Warburg impedance in solid AgI, which becomes dominant at low pI and pAg.[9,10]

The latter approach is easily understood if we assume that the total diffusion impedance (Warburg coefficient $\sigma$) consists of the diffusion impedance of reacting species in solid AgI ($\sigma_{AgI}$) and the diffusion impedance of reacting species in solution ($\sigma_{sol}$), so that:

$$\sigma = \sigma_{\mathrm{AgI}} + \sigma_{\mathrm{sol}} \tag{5}$$

Considering the limiting case for eqn. (5), we have:

(i) when pI or pAg is low, $\sigma_{\mathrm{AgI}} \gg \sigma_{\mathrm{sol}}$, so that $\sigma = \sigma_{\mathrm{AgI}}$

(ii) when pI or pAg is high, $\sigma_{\mathrm{AgI}} \ll \sigma_{\mathrm{sol}}$, so that $\sigma = \sigma_{\mathrm{sol}}$

The diffusion controlled interfacial ion-transfer on the Ag/AgI electrode can be written as:[1,8,10]

$$\mathrm{Ag^+_{sol}} \rightleftarrows \mathrm{Ag^+_{i}} \tag{6}$$

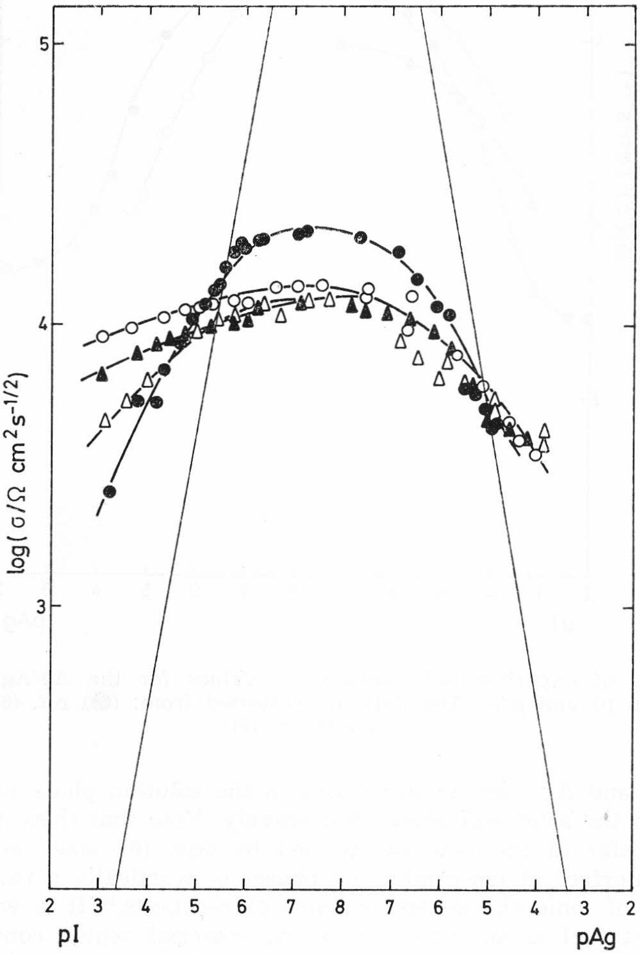

Figure 6. Log of experimentally obtained $\sigma$ values normalized to the apparent electrode area and corrected for the surface roughness factors $R_f$, for the Ag/AgI electrode of various thicknesses of the AgI-layer, in dependence on pI and pAg; (●) electrode 4a, $R_f = 1.9$; (△) electrode 4b, $R_f = 3.9$; (▲) electrode 4c, $R_f = 6.5$; (○) electrode 4d, $R_f = 9.2$.

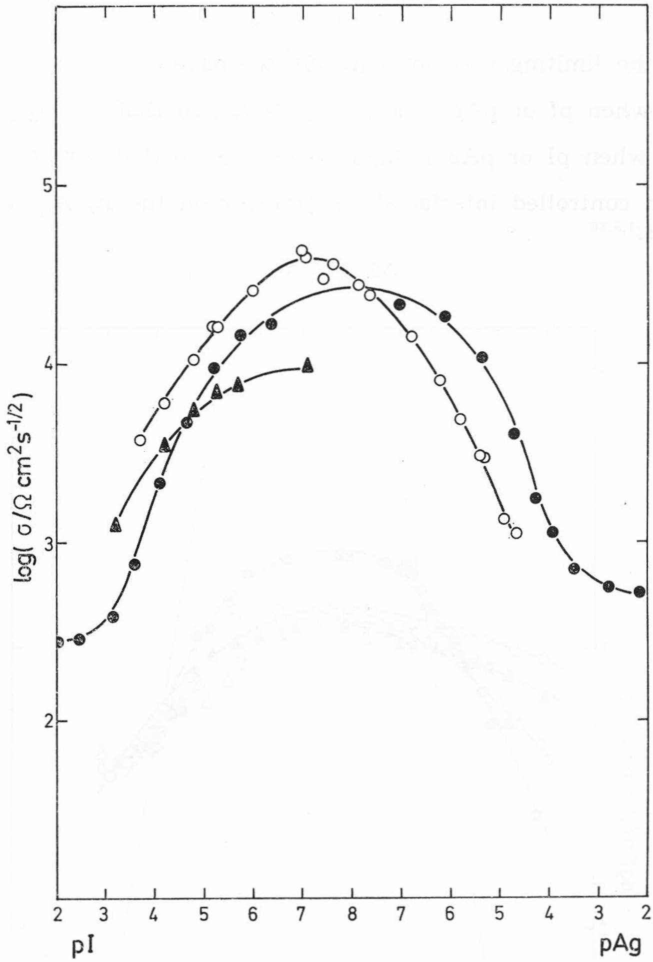

Figure 7. Log of experimentally obtained $\sigma$ values for the Ag/AgI electrode in dependence on pI and pAg. The data are collected from: (●) ref. (6); (▲) ref. (8); (○) refs. (9, 10).

where $Ag^+_{sol}$ and $Ag_i^+$ denote silver ions in the solution phase and interstitial silver ions in the solid AgI phase, respectively. Note that there is no classical electron transfer in the reaction defined by eqn. (6), since an ion-transfer across the interface of ion-conducting phases is practically a resolvation with conservation of ionic charge and valence of reactants.[14] It is worth pointing out here that AgI is an ionic conducting material which contains Frenkel deffects with silver ion interstitials ($Ag_i^+$) and silver ion vacancies ($\nu^-_{Ag^+}$), both mobile, but in much lower concentrations than $Ag^+$ ions situated in normal lattice sites.[15–21]

Since concentrations of both reacting species are variable in both phases[22], it appears that there is no close analogy between the metal-ion/metal electrode and Ag/AgI electrode. Taking this into account, it appears that the employment of eqn. (2) instead of eqns. (3) and (4) in the analysis of $\sigma$ values of the Ag/AgI electrode is more suitable. Consequently, the overall Warburg impedance should be considered as two Warburg impedances in series, where one pertains to the mass transfer polarization of the reacting species in the solid phase and the other in the solution phase. Also, according to eqn. (2), the overall $\sigma$ value could be considered as the sum of two particular $\sigma$ values, which has already been defined by eqn. (5). These considerations point to a greater similarity between the Ag/AgI electrode and amalgam electrodes where there are two components of variable concentrations in two phases. Although the observed deviations of $\sigma$ values, particularly in the low pI range, could in principle be explained by the above considerations, we could not end our discussion here, since the real existance of the classical Warburg behaviour in the solid AgI has not been sufficiently explained. Since both, $\mathrm{Ag}_i^+$ and $\nu^-_{\mathrm{Ag}^+}$ are mobile and responsible for conduction in AgI,[15-21] an analysis of the electrical behaviour of AgI based on description resulting from at least a two-ion treatment, would be appropriate here. Macdonald's works[23,24] showed that even in the case of intrinsically conducting solids with two mobile species, the overal cell impedance exhibits an explicit Warburg behaviour when: (i) charges of one sign are completely blocked, and (ii) charges of opposite sign are relatively free to discharge, but have much lower mobilities than those of blocked charges. Turning back to the electrolitically prepared AgI (references 1, 2, 9, 10 and the present work) and AgI prepared by reaction of silver substratum with $I_2$ vapour[3-8], one should not even think of a possibility to obtain an AgI sufficiently perfect and pure to exhibit an intrinsic conduction to a good approximation at 298 K. It is more reasonable that the equality of $\mathrm{Ag}_i^+$ and $\nu^-_{\mathrm{Ag}^+}$ concentrations is significantly affected by the presence of impurity ions and/or disorderly crystals. This is supported by the fact that a much higher specific conductivity of electrolitically prepared AgI[2,25-27] or »$I_2$-vapour plating« prepared AgI[5] in relation to pure single crystal AgI at room temperature[18,28,29] is observed, although a grain boundary conduction could contribute to higher conductivities as well.[19,26,28,29]

In the general extrinsic conduction theory, Macdonald[30] postulated that the classical Warburg concept should apply when the majority carriers are completely blocked, while the minority carriers are the only ones that can discharge.

On the basis of these considerations and the observed pI and pAg dependences of $\sigma$ values drawn in Figures 3—7, it seems that the predominant vacancies conduction case originated from cationic impurities and/or imperfections of crystals is the one that completely justifies the classical Warburg behaviour in the solid AgI, which is supported by the conductivity study[18], where it was postulated that $\mathrm{Ag}^+$ ion-vacancies are dominant charge carriers at temperatures lower than 353 K. Thus, the deviations of $\sigma$ values from those calculated by eqn. (4) could be explained by the influence of $\sigma_{\mathrm{AgI}}$, which at low pI and pAg becomes dominant in the overal $\sigma$ values or in the same range of magnitude like $\sigma_{\mathrm{sol}}$.

However, from Figures 3—7, it appears that at high pI and pAg, $\mathrm{pAg} > 5$, $\mathrm{pI} > 6$, where $\sigma = \sigma_{\mathrm{sol}}$, much lower $\sigma$ values in relation to those predicted by eqn. (4) are obtained, even when surface roughness factor is accounted for.

Although experimental shortcomings[6] or errors involved in graphical determinations of $\sigma$ values[8–10] could to some degree obscure the results, it seems reasonable to suppose that the origin of those deviations lies somewhere else. Eqns. (2—4) are derived for the equilibrium electrode potentials, and thus they are expressed in terms of bulk concentrations of the reacting species. It was recognized previously[9,10] that the specific adsorption process of $I^-$ ions up to the point of zero charge of solid AgI occurs at the Ag/AgI electrode interphase. This means that eqns. (2—4) apply most appropriately when the equilibrium electrode potential is coincident with the one of point of zero charge, which could be the reason why the normalization procedure taking into account the surface roughness factor gives the most reasonable results only in the restricted pAg range, where zero point of charge of AgI is located.[16,31] It was emphasized by the Sluyters,[32] however, that in the case of greater influence of reactant adsorption in the overall electrode reaction the intercepts $(2\sigma)^{-1}$ obtained from $Y'/\omega^{1/2}$ vs. $\omega^{1/2}$ dependences are much higher than predicted. The deviations were explained by the fact that the fitting procedure used converges to give $(2\sigma)^{-1}$ + part of $(2\sigma_a)^{-1}$, where factor $(2\sigma_a)^{-1}$ takes into account adsorption capacitance together with the kinetic parameter of adsorption. Turning back to our Ag/AgI electrode, the same explanation could be offered for systematically lower $\sigma$ values observed at high pI and pAg, just in the range where $I^-$ adsorption becomes prominent in the overall Ag/AgI electrode process.[9,10] As a consequence of two parallel and inseparable processes, diffusion controlled ion-transfer and diffusion controlled adsorption of $I^-$ ions, $\sigma$ values lower than predicted are obtained.

## CONCLUSIONS

The frequently observed differences between the experimentally obtained $\sigma$ values and those calculated by eqn. (4), could be explained by:

(i) the influence of diffusion polarization inside the solid AgI, which at low pI and pAg becomes dominant or in the same range of magnitude as that of the solution phase. Thus, at low pI and pAg, $\sigma$ values greater than predicted by eqn. (4) are observed,

(ii) the influence of specific adsorption of $I^-$ ions which at high pI and pAg becomes prominent in the overall electrode reaction. As a consequence, higher intercepts of $Y'/\omega^{1/2}$ vs. $\omega^{1/2}$ dependence, and thereby lower $\sigma$ values than predicted by eqn. (4) are obtained.

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## SAŽETAK

### O Warburgovu parametru Ag/AgI-Elektrode

*K. Kvastek i V. Horvat*

Razmatrani su mogući uzroci odstupanja izračunanih od eksperimentalno dobivenih vrijednosti Warburgova parametra Ag/AgI-elektrode. Nakon razmatranja potrebnih uvjeta za pojavu Warburgove impedancije u čvrstom AgI, sugerirano je da se ukupna Warburgova impedancija treba promatrati kao suma dviju Warburgovih impedancija u seriji, jedne u krutoj, a druge u tekućoj fazi. Razmatran je i utjecaj difuzno kontrolirane adsorpcije $I^-$ iona u paraleli s difuzno kontroliranim prijenosom iona na eksperimentalno dobivene vrijednosti Warburgovog parametra. Predloženo je da se u analizi Warburgove impedancije upotrebi teorijski pristup različit od onog, do sada korištenog u literaturi.