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Note on the Analysis of the Ag/AgI Electrode Impedance

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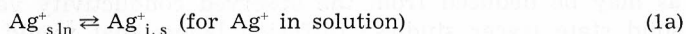University, De Dreijen 6, 6703 BC Wageningen, The Netherlands*

The impedance characteristics of the Ag/AgI electrode in
aqueous solution are discussed in terms of possible contributions
from the solid AgI. Distinction is made between pure crystalline
AgI and impure or doped AgI. Conditions for diffusional transport
of Ag^+ in the AgI phase are indicated and experimental studies
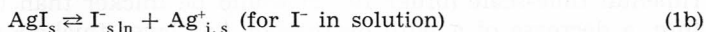are reconsidered in this respect.

DISCUSSION

Interpretation of the impedance (or admittance) spectrum of the silver/
/silver iodide electrode in aqueous solution has been a matter of dispute for
some time[1-4] and, considering the recent paper by Kvastek and Horvat,[5] it
stil is. There are a number of basic aspects which seem to obscure the discus-
sion and the present note is intended to point them out explicitly.

First of all, it will be useful to emphasize the distinction between
electrodes consisting of pure, crystalline AgI and electrodes incorporating
imperfect AgI, containing impurities. In the former case, the solid AgI will
expose its intrinsic conducting properties and an AgI electrode in a solution
of Ag^+ or I^- ions will be similar to a metal ion/metal electrode. The essential
charge transfer process at the AgI/solution interface is

$$Ag^+_{s\,ln} \rightleftarrows Ag^+_{i,\,s} \text{ (for } Ag^+ \text{ in solution)} \tag{1a}$$

or

$$AgI_s \rightleftarrows I^-_{s\,ln} + Ag^+_{i,\,s} \text{ (for } I^- \text{ in solution)} \tag{1b}$$

where subscript i denotes interstitial and sln and s refer to solution phase
and solid AgI phase, respectively. For a given temperature the bulk concen-
tration of interstitial silver ions is a constant and equal to the concentration
of vacancies $[V_{Ag^+}]^-$, as prescribed by the Frenkel defect equilibrium

$$Ag_i^+ + [V_{Ag^+}]^- \rightleftarrows [Ag^+_{AgI}]^\circ \tag{2}$$

Because of the applicability of (2), eqn (1a) can be alternatively represented
as

$$Ag^+_{s\,ln} + [V_{Ag^+}]^- \rightleftarrows [Ag^+_{AgI}]^\circ \tag{3}$$

which is fully analogous to e. g. $Ag^+ + e \rightleftarrows Ag$. It should be stressed that the
concentration of Ag^+ interstitials in AgI is an intrinsic property of the solid.

Only by doping the AgI, e. g. with divalent cations, the[Ag_i^+] becomes a variable and the analogy with the simple metal ion/metal electrode is lost.

The above considerations can be extended to the suitability of existing impedance/admittance expressions for the AgI electrode. The reversible metal ion/metal electrode will show simple Randles behavior, with a possible adsorption term included in the capacitive component. Therefore, the admittance equations employed by Kvastek and Horvat[2,3,5] can only be appropriate if the activity of the charge carrier in the solid (Ag_i^+) is an independent variable, that is if the AgI is doped or if it is appreciably impure. It may be added that only with the transport number of Ag^+ in the solid approaching zero, the conditions for diffusional transport of these ions in the phase are fulfilled[7] so that a corresponding Warburg term may be envisaged.

The nature of the experimental data makes it quite tempting to explain the observed impedance characteristics of the AgI electrode in terms of Warburg behavior of the transport processes inside the solid phase.[1,5] All experimental studies, in combination with various types of data analysis,[1-5] reveal a certain residual Warburg impedance. Nevertheless, it should be pointed out that experimental evidence contains some controversial elements. Some of the investigations[1,4] refer to crystalline γ-AgI film electrodes, for which it has been ruled out[8] that there would be a relatively high level of conducting impurities in the AgI. It may be added that even for the electrolytically prepared AgI electrodes, used in other studies,[2,3,5] the observed resistivity indicates a level of conducting impurities which is not more than one order of magnitude higher than for the crystalline γ-AgI.

That conditions for diffusion of Ag^+ in AgI may be not fulfilled is indicated by some additional observations. First, there is no real difference between the transport impedance of the crystalline AgI film electrode and the electrolytically prepared AgI electrode, suggesting that the nature of the solid does not really count here. Second, the recent data by Kvastek and Horvat[5] show that the overall Warburg parameter σ increases with decreasing the AgI layer thickness. If the layer is sufficiently thick to warrant semi-infinite linear diffusion (leading to Warburg behavior), then σ should be independent of layer thickness. Since the interstitial Ag^+ ions are very mobile, as may be deduced from the observed conductivity values[8] as well as from solid state tracer studies,[9] diffusion layers that would develop on the experimental time-scale (order 10^{-3} s) would be thicker than the AgI layer. Therefore, a decrease of σ with decreasing AgI layer thickness would be consistent with the picture of Ag^+ diffusion in the solid which is contradicted by the experimental data.

In spite of the objections raised, the question is why the AgI electrode »simulates« Warburg behavior. At this moment there is no definite answer to this question. However, some relevant observations can be put forward. First, a proper consideration of the roughness of the electrode surface[4] solves part of the problem. In a certain range of equilibrium potentials, i. e. those for an excess of Ag^+ in solution, refined admittance analysis leads to a satisfactory agreement between the measured overall σ and the Warburg parameter for the component in solution only. Furthermore, the observed frequency dependence of the admittance components may, at least on a qualitative level, be explained by surface roughness[4]. Also Kvastek and Horvat's recent data[5]

suggest that AgI surface roughness, rather than layer thickness, influences the observed admittance properties. A useful test would therefore be to dope the AgI layer with known amounts of e. g. divalent ions and to check whether the admittance contains contributions from diffusion of Ag^+ in the solid.

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SAŽETAK

Analiza impedancije Ag/AgI-elektrode

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Raspravlja se o mogućem doprinosu AgI(s) na impedancijska svojstva Ag/AgI-elektrode u vodenoj otopini. Naznačeni su uvjeti za difuzijski prijenos Ag^+-iona u AgI-fazi i u tome smislu ponovno razmotrena eksperimentalna istraživanja.