CROATICA CHEMICA ACTA CCACAA **60** (4) 709—716 (1987)

YU ISSN 0011-1643
CCA-1768 UDC 546.57
Note

Once More About the Analysis of the Ag/AgI Electrode Impedance

K. Kvastek and V. Horvat

Center for Marine Research and Department of Physical Chemistry, »Rudjer Bošković« Institute, 41001 Zagreb, POB 1016, Croatia, Yugoslavia

Received April 27, 1987

The reliability of different electrode admittance equations in the case of the Ag/AgI electrode is critically discussed. It is shown that the admittance equation already derived for the metal amalgam/metal-ion reversible electrode reaction coupled with reactant adsorption offers some advantages compared to the admittance equation for the reversible electrode reaction on the metal/metal-ion electrode.

New results of impedance measurements of the Ag/AgI electrode are reported.

In the paper *Note on the Analysis of the Ag/AgI Electrode Impedance Data*[1], H. P. van Leeuwen stressed some points for discussion which came up following the publication of a number of papers on the analysis and interpretation of the Ag/AgI electrode impedance data.[2–7] In particular, he comments on the possibility of diffusion in solid AgI, which has been recently postulated[7] as a possible cause of commonly observed deviations from calculated and experimentally obtained values of the Warburg parameter. The existence of Warburg behaviour in solid AgI arises as a natural consequence of the physical model used for the analysis. This was chosen by applying several diagnostic criteria for the recognization of influence of various processes in the overall electrode response.[4,5] It has been shown that the experimental data agree well with the model otherwise proposed for the general case of a reversible electrode reaction coupled with strong reactant adsorption.[8,9] The corresponding electrode admittance equation may be written as follows:

$$Y = \omega^{1/2}(1 + i)/2\sigma + \omega\,(C_{LF} - C_{HF})\,[u + i\,(u + 2)/(u^2 + 2u + 2)] + i\omega C_{HF} \qquad (1)$$

where Y denotes complex admittance, while w and i are angular frequency and $\sqrt{-1}$, respectively. According to Eqn. (1), the interfacial (electrode) admittance is the sum of three parallel admittances: 1) classical Warburg admittance; 2) adsorption admittance, and 3) the admittance due to high frequency capacitance. Four frequency independent parameters, Warburg parameter σ, adsorption capacitance ($C_{LF} - C_{HF}$), $u' = u/\omega^{1/2}$ and C_{HF} describe the total system. The parameters are defined as follows:[8,9]

$$\sigma = (RT/n^2 F^2 2^{1/2})\,(1/C_0 D_0^{1/2} + 1/C_r D_r^{1/2}) \qquad (2a)$$

$$C_{LF} = [\partial\,(q + nF\Gamma_0)/\partial E]_\psi - nF\,(\sigma_r/\sigma)\,[\partial\,(\Gamma_0 + \Gamma_r)/\partial E]_\psi \qquad (2b)$$

$$u' = u/\omega^{1/2} = 2^{1/2}\,[\partial\,(\Gamma_0 + \Gamma_r)/\partial\,\psi]_E \tag{2c}$$

$$C_{HF} = [\partial\,(q + nF\Gamma_0)/\partial E]_{\Gamma_0+\Gamma_r} \tag{2d}$$

with ψ defined as $\psi = C_o\,D_o^{1/2} + C_r\,D_r^{1/2}$

Here, C and D denote concentration and diffusion coefficient of reacting species, Γ is surface excess of adsorbing species, E is potential, while other symbols have their usual meanings.

In the equivalent circuit notation, Eqn. (1) is given in Figure 1.

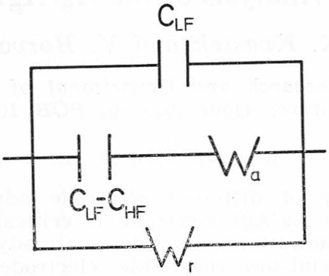

Figure 1. Equivalent circuit for the general case of a reversible electrode reaction coupled with a strong reactant adsorption defined by Eqn. (1). The subscripts to the Warburg symbols denote diffusion of (a)dsorbing and (r)eacting species.

The equivalent circuit in Figure 1 is reduced to the Randles circuit (with no charge transfer resistance) if there is no adsorption, if there is weak reactant adsorption or, if there is reversible metal/metal-ion electrode reaction. In the third case, Eqn. (1) reduces to the following equation, already used in the analysis of the Ag/AgI electrode impedance data[6]:

$$Y = \omega^{1/2}\,(1 + i)/2\sigma + i\omega C_{LF} \tag{3}$$

with

$$\sigma = (RT/n^2\,F^2 2^{1/2})\,(C_o D_o^{1/2})^{-1} \tag{4a}$$

$$C_{LF} = d\,(q + nF\Gamma_o)/dE \tag{4b}$$

The equivalent circuit which corresponds to Eqn. (3) and which is in fact a low frequency limit of the more general one in Figure 1, is drawn in Figure 2.

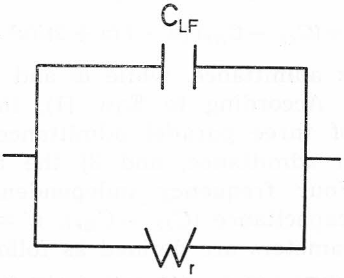

Figure 2. Equivalent circuit for reversible metal/metal-ion electrode reaction, defined by Eqn. (3).

There are three main points which support the use of Eqn. (1) and equivalent circuit in Figure 1 in the analysis of the Ag/AgI electrode impedance data:[4,5]

i) there is a strong decrease of experimentally obtained $\omega^{1/2}/Y'$ *vs.* $\omega^{1/2}$ dependence, while $\omega^{1/2}/Y'$ should be independent on ω if Eqn. (3) and equivalent circuit in Figure 2 were true;

ii) the complex capacitance dispersion exhibits circular shapes at higher frequencies, followed by straight lines (slope near $\pi/4$) at lower frequencies. The complex capacitances should be straight lines with slopes of $\pi/4$ in the whole frequency range if eqn. (3) and equivalent circuit in Figure 2 were true;

iii) the experimentally obtained values for the Warburg parameter σ are not in agreement with σ values calculated by use of Eqn. (4a).

The point i) was discussed by Polder and co-workers[6] who obtained different impedances for differently prepared Ag/AgI electrodes. The results are explained in terms of the so called »macroscopic surface roughness«, since it was shown that I_2-vapour-plating electrode, looking smooth on SEM pictures, behaves like a reversible metal/metal-ion electrode, i. e. according to the Eqn. (3), while electrolytically prepared Ag/AgI electrode, which looks »rough« on SEM picture, deviates from this behaviour.

The decrease of $\omega^{1/2}/Y'$ *vs.* $\omega^{1/2}$ obtained for »rough« electrodes is explained by the size of irregularities and frequency range used, and it was stressed that the agreement with Eqn. (1) was only accidental.

This explanation, however, could not account for either the systematic presence of circles in the complex capacitance plane (point ii)) (straight lines of $\pi/4$ slopes should be obtained for any roughness), or the strong influence of the concentration of electroactive species on the estimated surface roughness factors from $\omega^{1/2}/Y'$ dependences. In addition, most recent results[10] show that, if experiments are performed on differently prepared Ag/AgI electrodes with constant surface roughness, differences in impedance are obtained too, particularly in the ranges where decrease in $\omega^{1/2}/Y'$ *vs.* $\omega^{1/2}$ or circular shapes in complex capacitance dispersion becomes significant. The results are summarized in Figures 3—6.

While SEM pictures in Figure 3 indicate nearly the same roughness of two electrodes, X-ray diffraction patterns in Figure 4 indicate different crystal structures of two electrodes, i. e. electrode A exhibits mainly β-structure, while electrode B shows predominance of γ-structure. In Figure 5, $\omega^{1/2}/Y'$ *vs.* $\omega^{1/2}$ dependences are drawn, which indicate that different electrodes exhibit different character in different frequency ranges. The same is obvious in Figure 6, where circular arcs become prominent at different frequencies. The results can be explained on the basis of different adsorption parameters u' and $(C_{LF} - C_{HF})$ arising from different crystal modifications of Ag/AgI electrodes. In relation with point iii), it has recently been stated,[7] that Eqn. (2a) is more reliable for the calculations of σ values for the Ag/AgI electrodes, than the commonly applied Eqns. (4b)[2-6] because, for certain range of I^- concentrations, Eqn. (2a) accounts for higher σ values experimentally obtained. The use of Eqn. (2a) suggests the similarity between the Ag/AgI electrode

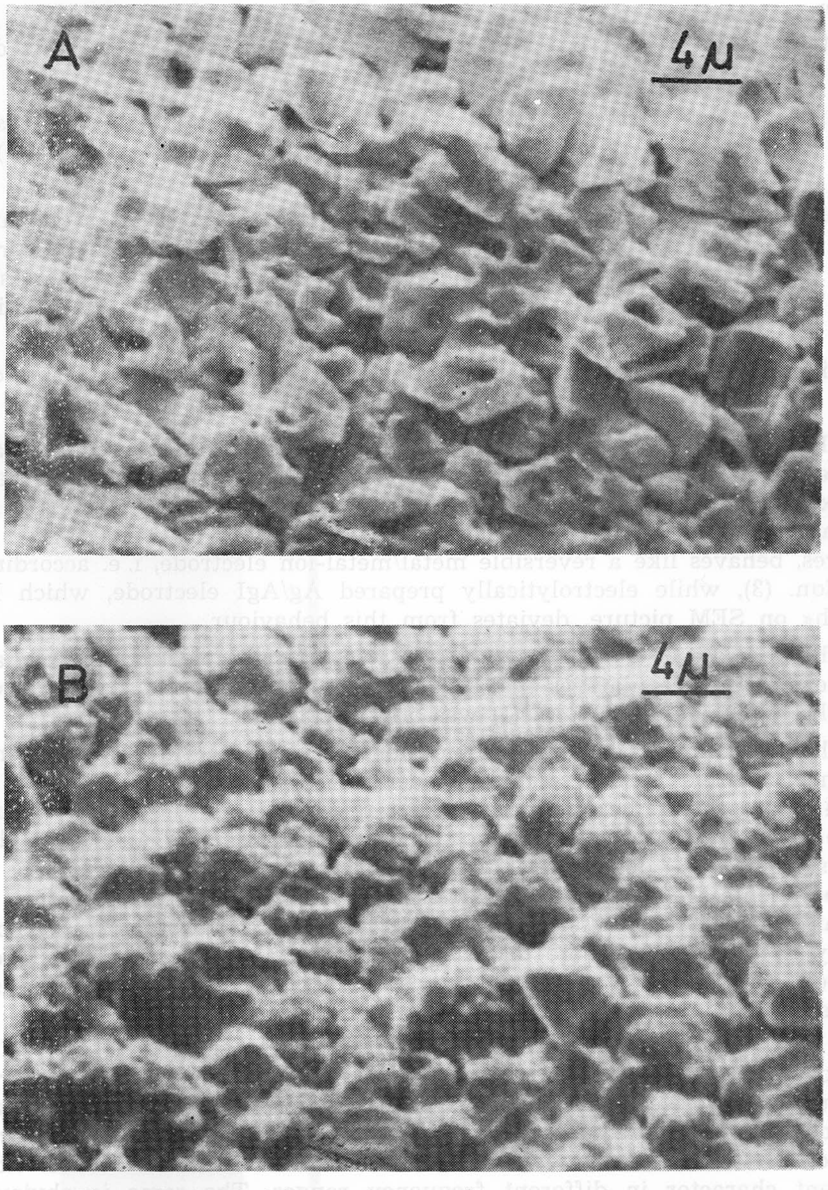

Figure 3. SEM pictures of the Ag/AgI electrodes A and B.

and a metal amalgam/metal-ion electrode, while the use of Eqn. (4b) is based on the analogy to metal-metal-ion electrode.

The principal charge transfer when either I^- ions or Ag^+ ions are in excess in the electrolyte solution, may be written as:

$$Ag^+_{sol} \rightleftharpoons Ag_i^+ \qquad (5)$$

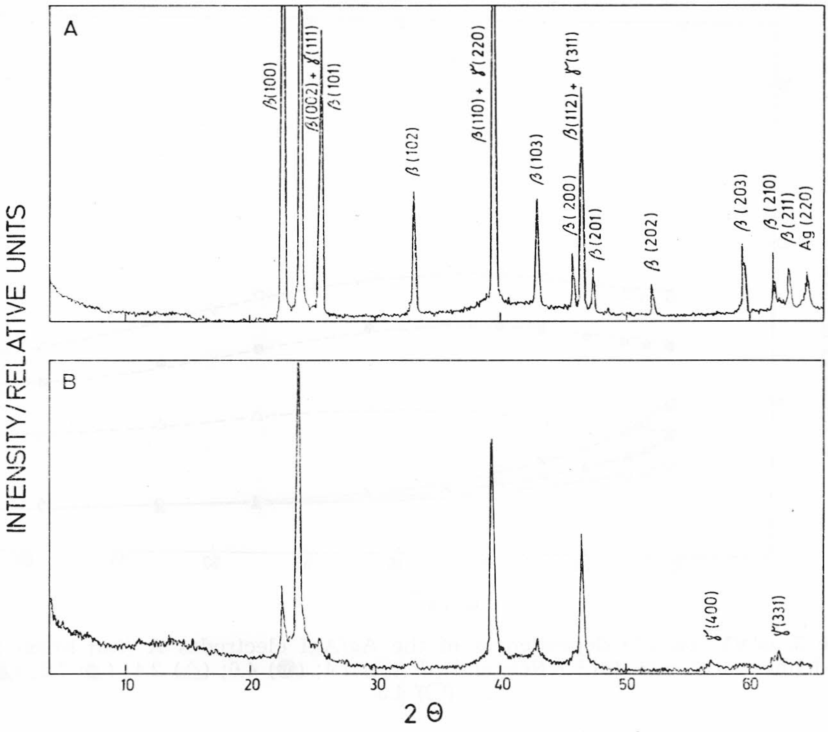

Figure 4. X-ray diffraction patterns of the Ag/AgI electrode A and B.

where Ag_i^+ denotes interstitials in AgI solid phase. Now, if Ag^+ ions are in excess, due to Frenkel defect equilibrium

$$Ag_i^+ + (v^-) \rightleftharpoons Ag^o_{latt} \tag{6}$$

where (v^-) are silver ion vacancies, the overall reaction becomes:

$$Ag^+_{sol} + (v^-) \rightleftharpoons Ag^o_{latt} \tag{7}$$

On the other hand, if I^- ions are in the excess, due to solubility product equilibrium:

$$Ag^+_{sol} + I^-_{sol} \rightleftharpoons AgI \tag{8}$$

the overall reaction becomes:

$$Ag_i^+ + I^-_{sol} \rightleftharpoons AgI \tag{9}$$

It must be pointed our here, that any interaction between aqueous ions (Ag^+_{sol} and I^-_{sol}) and lattice deffects (Ag_i^+ and v^-) is indirect, occuring through equilibrium reactions (6) and (8). Although the formal similarity between the overall reactions (7) and (9) and classical metal/metal ion electrode reaction

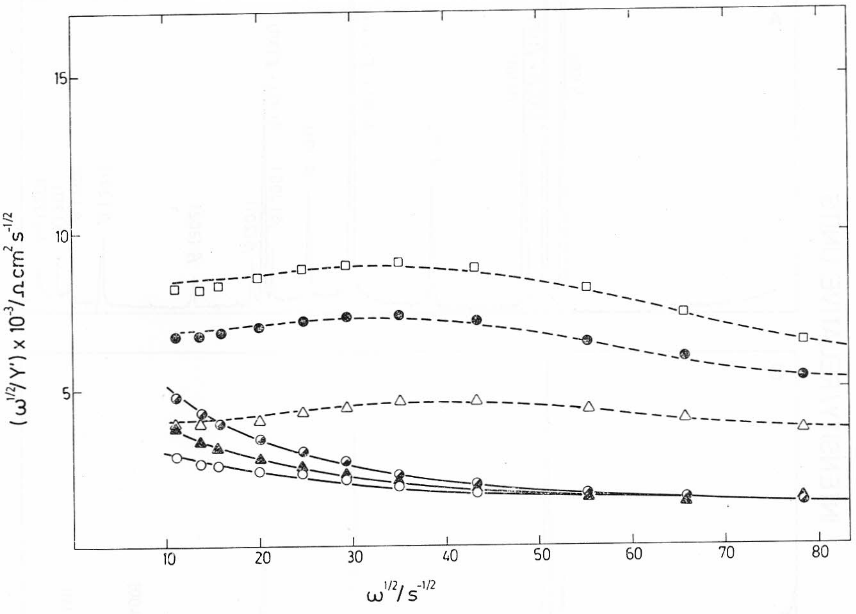

Figure 5. $\omega^{1/2}/Y'$ *vs.* $\omega^{1/2}$ dependences of the Ag/AgI electrodes A (full lines) and B (dotted lines), 0.01 mol dm^{-3} KNO_3 and *pI*: (□) 7.4; (●) 4.0; (△) 2.4; (◐) 7.2; (▲) 4.9; (○) 4.3.

$M^{n+} + ne \rightleftharpoons M$ realy exists because of concentration-invariable products (Ag^{o}_{latt} and AgI), it must be stressed that two independent variables are still to be considered, since neither concentration of Ag_i^+ nor concentration of ν^- has to be considered invariable by definition. The same was stressed by Honig[11] and Hoffman.[12] Other conditions for diffusion impedance in solid AgI were discussed in details elsewhere,[7] where it was stated that vacant mobility extrinsic situation, which is normal for room temperature AgI,[13] may fully explain the Warburg behaviour in solid AgI. We do agree that good experiments, performed on doped AgI as it has already been suggested,[1,7] as well as the experiments on single crystals of AgI will give better answers to this problem.

According to the authors' opinion, both models — the one given in Figure 2 and defined by Eqn. (3), as well as that given by Eqn. (1) and Figure 1, — are too simple to give a faithful description of such a complicated system as Ag/AgI electrode. It seems, however, that *up to now* the model given by Eqn. (1) and Figure 1 fits the largest amount of experimental data and could therefore be considered as a better approximation.

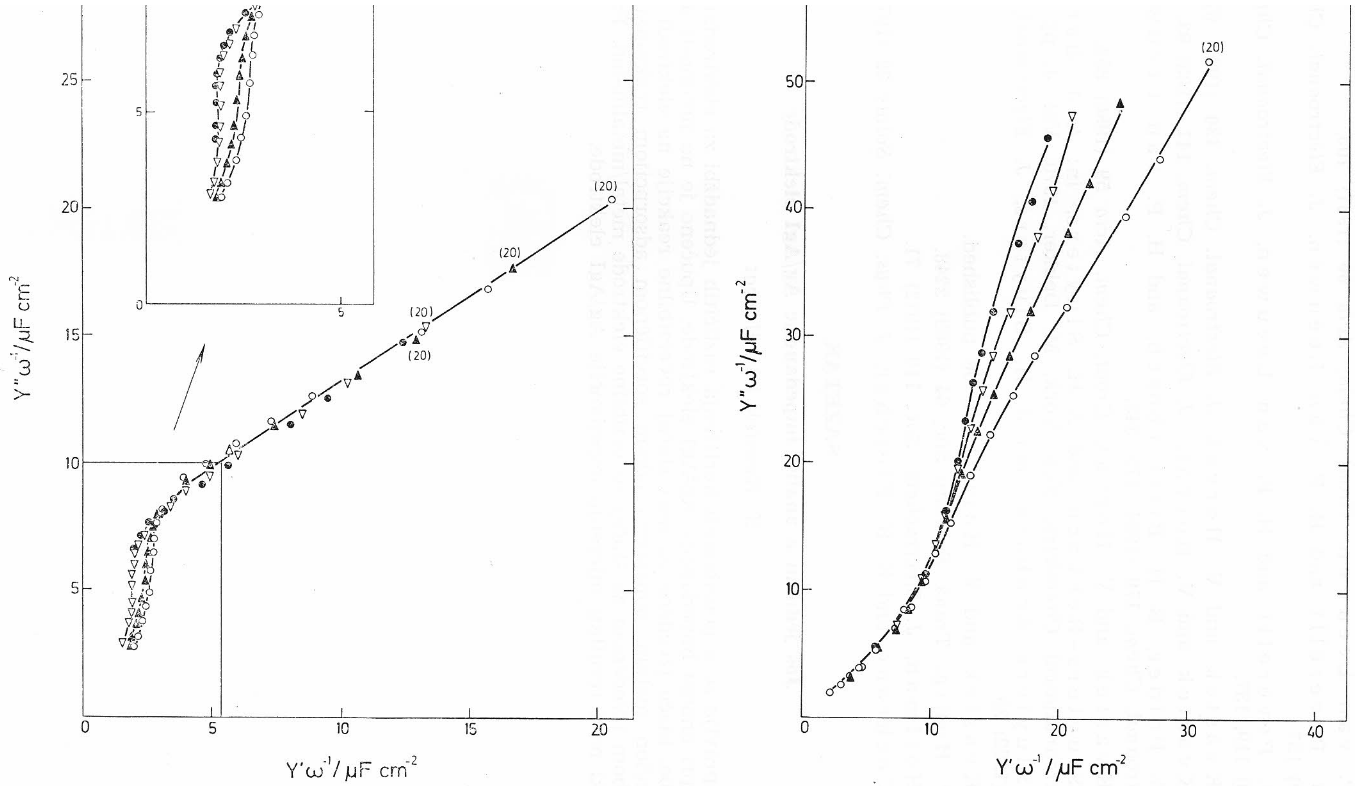

Figure 6. Complex capacitance dispersion for the Ag/AgI electrodes as a parametric function of frequency, in 0.01 mol dm^{-3} KNO_3. Electrode A, pI = (○) 4.3; (▲) 4.9; (▽) 5.5; (●) 7.2. Electrode B, pI = (○) 2.8; (▲) 3.4; (▽) 4.7; (●) 5.8. Frequency range: 20 Hz — 20 kHz.

REFERENCES

1. H. P. van Leeuwen, *Croat. Chem. Acta* **60** (1987) 705.
2. K. J. Peverelli and H. P. van Leeuwen, *J. Electroanal. Chem.* **99** (1979) 157.
3. K. J. Peverelli and H. P. van Leeuwen, *J. Electroanal. Chem.* **110** (1980) 119, 137.
4. K. Kvastek and V. Horvat, *J. Electroanal. Chem.* **130** (1981) 67.
5. K. Kvastek and V. Horvat, *J. Electroanal. Chem.* **147** (1983) 83.
6. R. B. Polder, B. H. Bijsterbosch, and H. P. van Leeuwen, *J. Electroanal. Chem.* **170** (1984) 175, 343.
7. K. Kvastek and V. Horvat, *Croat. Chem. Acta* **59** (1986) 853.
8. M. Sluyters-Rehbach and J. H. Sluyters, in: A. J. Bard (ed), *Electroanalytical Chemistry,* New York, M. Dekker, 1970, Vol. 4, pp. 1—128.
9. M. Sluyters-Rehbach and J. H. Sluyters, *J. Electroanal. Chem.* **136** (1982) 39.
10. K. Kvastek and V. Horvat, to be published.
11. E. P. Honig, *Trans. Faraday Soc.* **64** (1969) 2248.
12. A. Hoffman, *J. Electrochem. Soc.* **119** (1972) 71.
13. G. Cochrane and N. H. Fletcher, *J. Phys. Chem. Solids* **32** (1971) 2557.

SAŽETAK

Još jednom o analizi impedancije Ag/AgI elektrode

K. Kvastek i V. Horvat

Raspravlja se o pouzdanosti korištenja različitih jednadžbi za elektrodnu admitanciju pri analizi impedancije Ag/AgI elektrode. Upućeno je na prednosti upotrebe jednadžbe, inače izvedene za opći slučaj reverzibilne reakcije na elektrodi metalni amalgam/ion metala, popraćeno jakom specifičnom adsorpcijom reaktanata, pred jednadžbom izvedenom za slučaj reverzibilne elektrode metal/metalni-ion. Prikazani su i neki novi rezultati mjerenja impedancije Ag/AgI elektrode.