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The Influence of the Experimental Setup Upon the Modelling of the Impedance Spectra in Molten Salts*

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To settle the frequently raised problem of the influence of cell geometry on the value of the evaluated by the electrochemical impedance spectroscopy (EIS) double layer capacitance, in this paper two types of cells have been tested in two and three electrodes experiments in molten salts. In the first type cell, the working silver electrodes were immersed directly in the molten NaCl – KCl eutectic mixture at 700°C, while in the second type cell, the working silver electrodes were placed inside quartz tubes connected to the bulk melt by a small hole. The only effect of the quartz tube was the desired increase of the electrolyte resistance from 0.7 Ω to 5.5 Ω, which is important in lowering the ac measuring current of the Solartron 1260 Phase Gain Analyser. The evaluated values of the double layer capacitance were to experimental uncertainty the same in both cells. It can be thus concluded, that the frequently raised in aqueous electrolytes problem of the influence of the cell geometry upon the values of the evaluated double layer capacitance, in molten salts does not lead to any significant errors. This is presumable due to the fact that the conductivity of molten salts is usually two order higher than aqueous electrolytes, and the corresponding ohmic drops are much smaller.

Key words: molten salts, silver electrode, double layer capacitance, polarizable electrode, electrochemical impedance spectroscopy

So far the influence of the different forms of the cell construction on the evaluation of the impedance spectra was studied on ideal polarized mercury drop electrode in aqueous solutions. Grahame has used different forms (not described) of the apparatus [1], stating however that in the typical three electrodes arrangement, in which the dropping mercury electrode was inside a large (few cm^2) platinum foil (serving as an auxiliary electrode) and the reference electrode connected to the cell by a glass tube, gave the best performance in the rather low frequency range used (240 Hz to 5000 Hz). In the summary of his paper, Grahame concluded, that "significant errors arise in the measurement of capacity and the resistance when the electrical resistance from every element of the surface to the reference electrode is not the same". His measurements have been, however, performed in aqueous electrolytic solutions, in which the electrolyte resistance is much larger than in molten salts.

There are two main differences between the aqueous electrolytes and molten salts. First, molten salts do not have solvent molecules, which cover the metallic

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

electrode and create primary hydration shell. Second, the conductance of molten salts is 2 to 3 orders higher than those of aqueous electrolytic solutions and consequently the voltage drop on the molten electrolyte resistance due to the current flow is negligible.

The purpose of this work is to check the influence of the geometry of the experimental impedance cells in two and three electrodes arrangement, upon the value of the evaluated double layer capacitance. Solid silver electrode in pure molten eutectic NaCl – KCl (no silver ions added) has been used in two cell geometry arrangements.

EXPERIMENTAL

Materials. Metallic silver of spectral purity (BDH, UK) was cleaned from the surface oxides layer. The following salts, used in experiments: sodium chloride p.a. (POCH Gliwice, Poland), potassium chloride p.a. (POCH Gliwice, Poland), were dried in 200°C under a stream of dry nitrogen for 12 hours.

Apparatus and procedure. The impedance spectra were recorded in two types of experiments. In the first experiment no outer potential was applied to the working lead electrode. The measuring vessel used in this two-electrode experiments, presented in Fig. 1a, consisted of an alumina crucible filled with molten eutectic mixture of NaCl – KCl, was placed in a quartz tube, closed with the brass lid. Two identical silver electrodes, each of 0.25 cm^2 of geometric surface area, were connected in series to the Solartron 1260 Phase Gain Analyzer. The temperature was measured by the PtRh-Pt thermocouple immersed in the melt and an inert atmosphere was maintained by flow of dry nitrogen. The vessel was placed in an electrically heated furnace, with the temperature control within 1 degree and a stability *ca* 0.1°C. Measurements were performed within the 10 Hz ÷ 500 kHz frequency range at 700°C. The cell presented in Fig. 1b, in which the same two silver electrode were placed inside quartz tubes, was used to increase the electrolyte resistance. Such cell arrangement was used to settle the question, whether the cell geometry will or not influence the determination of the double layer capacitance by the electrochemical impedance spectroscopy (EIS).

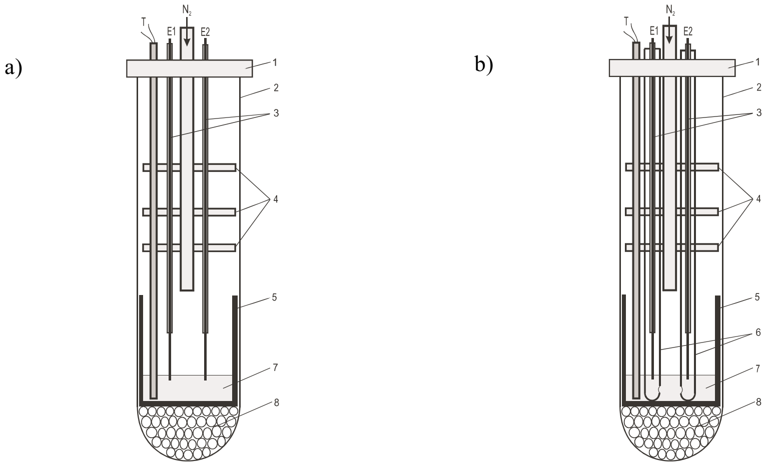

Figure 1. The measuring cells applied in two-electrode impedance measurements. 1 – brass lid; 2 – quartz tube; 3 – silver wires in alumina insulation; 4 – alumina shields lowering IR radiation; 5 – alumina crucible; 6 – quartz tubes closed at the bottom; 7 – molten salt; 8 – ceramic beads; N$_2$ – nitrogen inlet; T – thermocouple; E1, E2 – identical silver electrodes.

The second type of experiments was a typical potentiostatic measurement in a three electrode configuration. In this experiment performed in the cells presented in Fig. 2, only one silver working electrode was used. The auxiliary electrode constituted a spectrally pure graphite rod pressed into an alumina tube and connected to a platinum wire. A porous pythagoras alumina tube containing 1 mole % solution of lead chloride in a NaCl – KCl eutectic mixture and a layer of lead at the bottom served as the reference electrode.

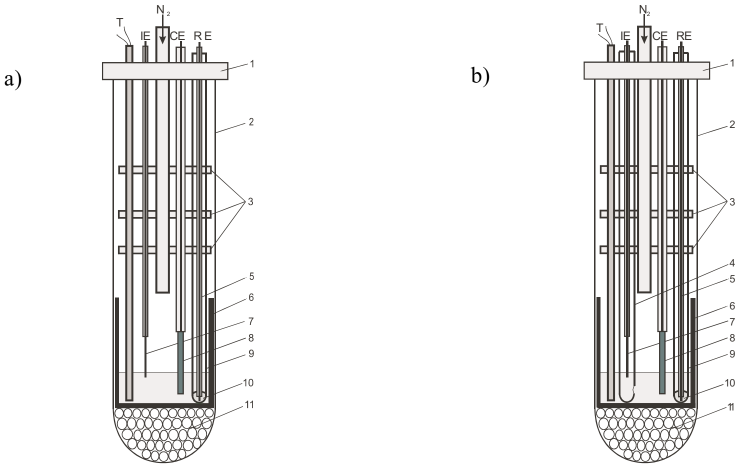

Figure 2. The measuring cells applied in three-electrode impedance measurements. 1 – brass lid; 2 – quartz tube; 3 – alumina shields lowering IR radiation; 4 – quartz tube closed at the bottom; 5 – molybdenum wire in alumina insulation; 6 – alumina crucible; 7 – silver wire in alumina insulation; 8 – graphite rod in alumina insulation; 9 – porous alumina tube filled with lead salt solution; 10 – molten lead layer; 11 – ceramic beads; N_2 – nitrogen inlet; T – thermocouple; IE – indicator; RE – reference; CE – counter electrodes.

EQUIVALENT CIRCUITS

Although the silver electrode immersed in pure molten NaCl – KCl eutectic mixture (no Ag^+ cations added) was supposed to be an ideally polarizable electrode, it appears, that it undergoes a small spontaneous dissolution (compare the voltammetric curve presented in Fig. 5) and the faradaic current was present. The impedance spectra recorded in the frequency range from 10 Hz to 500 kHz show thus inductive behaviour [2,3]. Therefore the equivalent circuits for the modelling of the recorded impedance spectra presented in Fig. 3 must contain, apart from the outer inductance, electrolyte resistance and double layer capacitance, also a charge transfer resistance and double layer inductance. The presence of double layer inductance was up to now found in high energy electrodes in molten salts, with large exchange current densities [4–7]. It appears, however, that even small exchange current present at the silver electrode immersed into molten NaCl – KCl eutectic mixture, due to the above mentioned small spontaneous anodic dissolution of the silver, results in the appearance of the double layer inductance and the diffusion Warburg impedance.

The equivalent circuit used for the modelling of the impedance spectra in the cell 1 (two silver electrode configuration) is presented in Fig. 3a.

It is known in the theory of the EIS, that the measured cell impedance is equal to the impedance of the working lead electrode only, if the impedance of the auxiliary electrode (in our case a graphite rode) can be neglected. In our experiments this is not the case, as the impedances of both working and auxiliary electrodes are small and comparable. So the equivalent circuit must contain also elements, which models the auxiliary electrode. The constant phase element loop (Fig. 3b) accounts well for the impedance of the porous graphite electrode.

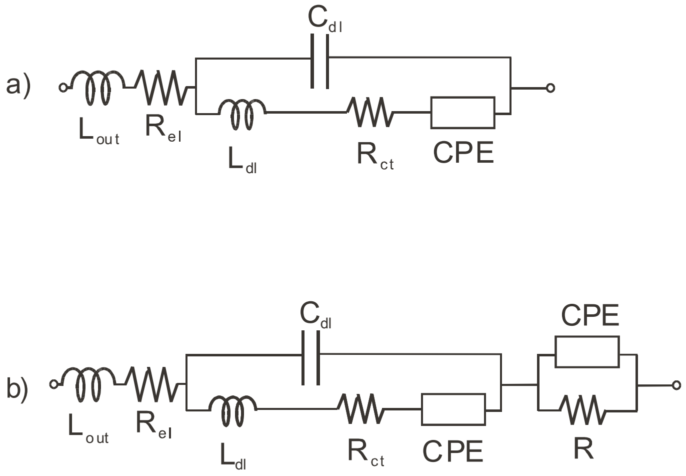

Figure 3. Equivalent circuits used. Description in the text.

RESULTS AND DISCUSSION

Two electrode experiments. From obvious reason, the impedance spectra in the two electrode experiments have been recorded using only Solartron Phase Gaine Analyzer 1260 at the rest potential in the frequency range from 10 Hz to 500 kHz. The typical impedance spectra and their NLLSFit (non linear least squares fit), according to the equivalent circuit presented in Fig. 3a, are shown in Fig. 4. Although the number of recorded frequencies for each spectrum was always 200 points, only some points are shown in the below figures, to distinguish between the experimental points (markers) and the NLLSFit (line).

The main difference between these two impedance spectra is the value of the electrolyte resistance (0.7 Ω and 5.5 Ω) respectively. The values of the evaluated double layer capacitance, however, in these two experiments are the same within experimental errors: $3.00\pm0.72\,\mu\text{F cm}^{-2}$ in cell 1a and $2.91\pm0.89\,\mu\text{F cm}^{-2}$ using the cell 1b.

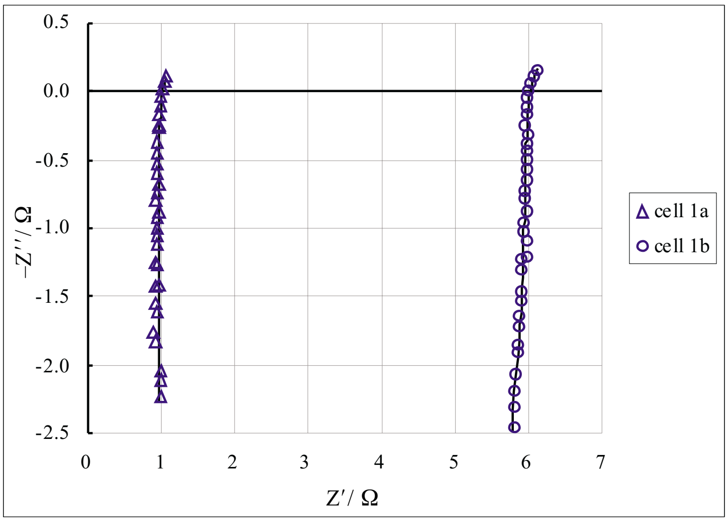

Figure 4. The impedance spectra of the Ag electrode in two electrode experiment. Markers – experimental points, lines – NLLSFit.

Three electrode experiments. Before recording of the impedance spectra of the Ag electrode in the molten NaCl – KCl eutectic mixture at several potentials, a linear voltammetric curve has been recorded from 0.15 V (against lead reference electrode in the same melt) to –1.70 V. It follows from a typical recording presented in Fig. 5 that there are two potential ranges with a faradaic processes.

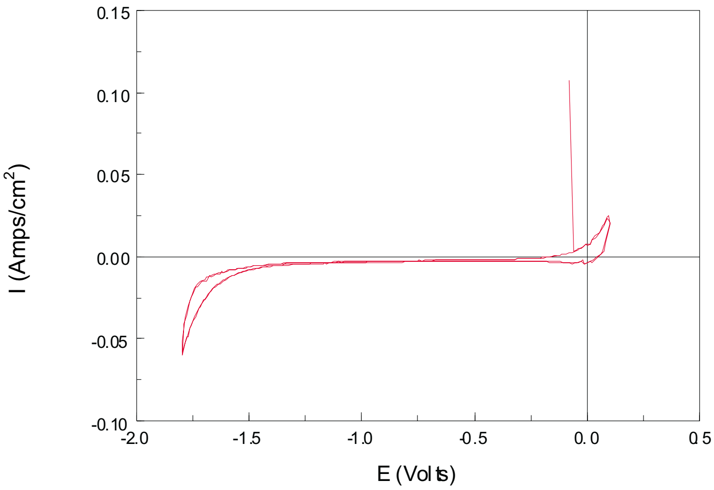

Figure 5. Linear sweep voltammogram of the Ag electrode in molten NaCl – KCl eutectic mixture at 700°C. Sweep rate 0.1 V/s.

At the far end of the negative potential (–1.7 V) the cathodic reduction of the Na^+ cations takes place with the formation of a Ag-Na amalgam

$Na^+ + e^- = Na$ (in Ag)

At the far positive end (0.15 V) of the potential range used, the dissolution of metallic silver takes place, with the formation of Ag^+ cations in the vicinity of the solid silver electrode

$Ag = Ag^+ + e^-$

In that way the polycrystalline solid Ag electrode, being rough anyhow, become even more rough.

The shape of the recorded impedance spectra varies with the potential. The 37 impedance spectra in a one measuring series were recorded starting from –1.7 V to 0.0 V (*versus* reference electrode) in 0.05 V steps and in the frequency range from 10 Hz to 100 kHz.

Examples of impedance spectra recorded in the cell 2a are presented in Fig. 6, while similar spectra recorded in the cell 2b are shown in Fig. 7. Markers represent experimental points, while the solid lines represent the NLLSFits by the equivalent circuits presented in Fig. 3.

Indeed, it is seen in Fig. 6 and Fig. 7, that at the high cathodic polarization and at anodic polarization, the impedance spectra show pronounced inductive behaviour, while in the potential range between these extreme values, the impedance spectra show more capacitive features. While the inductive impedance spectra in the far ends of the cathodic and anodic polarization potential can be modelled by the equivalent circuit presented in Fig. 3a (frequency range from 5 kHz to 100 kHz, where 100 kHz is the upper frequency limit of the 1287 Solartron Interface), the fitting of the impedance spectra of the silver electrode in the whole frequency range was only possible by the equivalent circuit presented in Fig. 3b, with a constant phase element (CPE) loop. The modelling was performed by the Boukamp's program [8] and checked with the Zview program of Mac Donald [9]. The agreement was very good in all cases. In that way the capacitance of the silver electrode in the chloride melt was evaluated as a function of potential for the experiments performed in cell 3a and 3b. The results are presented in Fig. 8 and Fig. 9 respectively.

The comparison of Figures 8 and 9 indicates clearly, that to the experimental uncertainty (± 10%), these two double layer capacitance – potential dependences are identical. We must thus conclude, that the placement of the silver working electrode inside a quartz tube, which may suggest unequal current distribution on a working electrode surface, does not influence the evaluation of the double layer capacitance. This is of course only true in molten salts, where the potential drops on the very low electrolyte resistance are negligible.

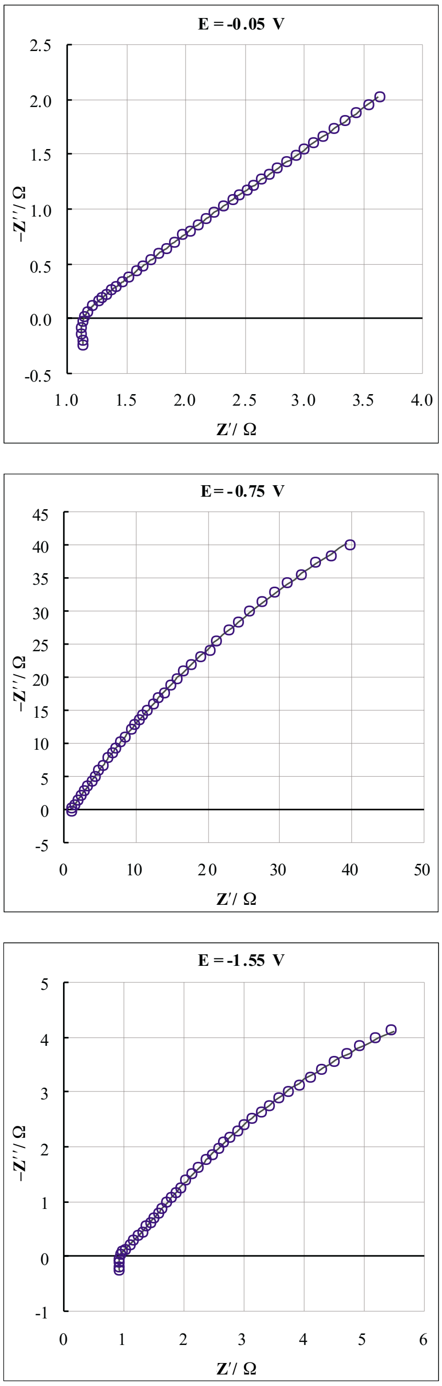

Figure 6. Impedance spectra in three electrode cell 2a at several potentials. Markers – experimental points, lines – NLLSFit.

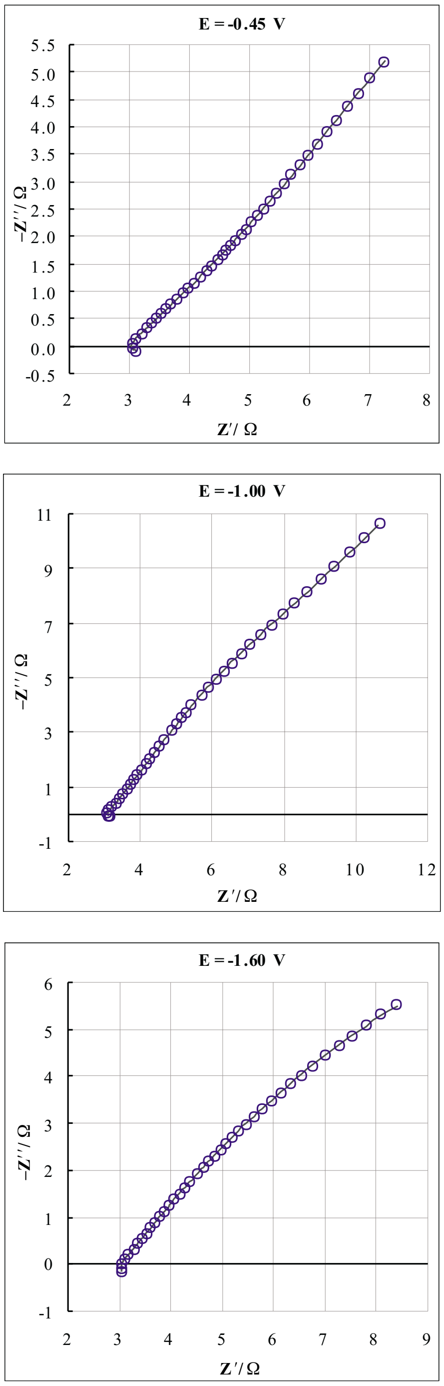

Figure 7. Impedance spectra in three electrode cell 2b at several potentials. Markers – experimental points, lines – NLLSFit.

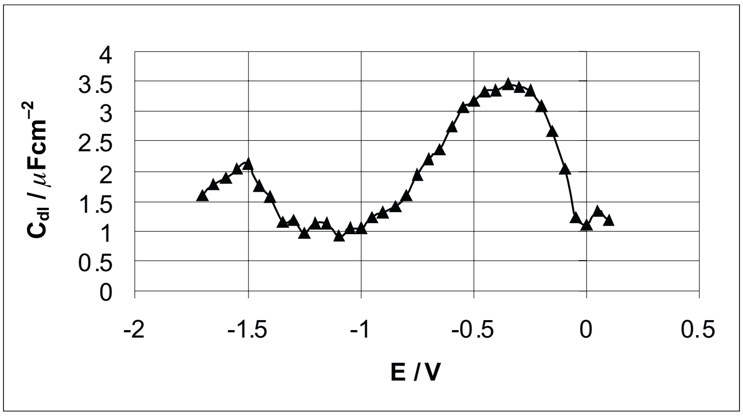

Figure 8. The potential dependence of the double layer capacitance of the silver electrode in the molten NaCl – KCl eutectic mixture at 700°C in the cell 2a.

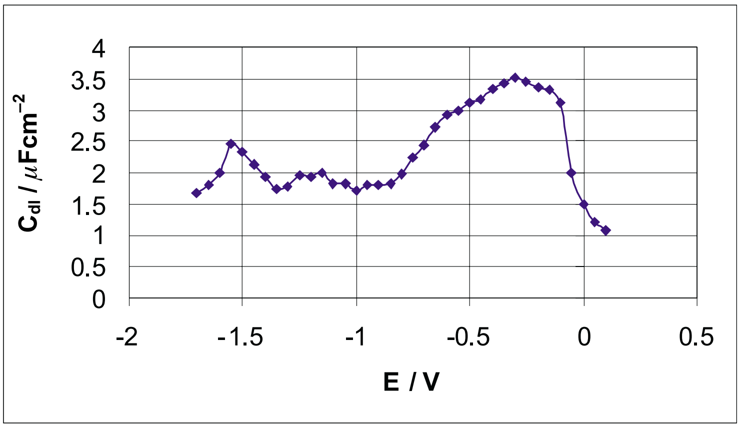

Figure 9. The potential dependence of the double layer capacitance of the silver electrode in the molten NaCl – KCl eutectic mixture at 700°C in cell 2b.

The origin of the capacitance picks on the double layer capacitance – potential curves has been already explained in another paper [7] but one should comment on the two different capacitance picks heights in Figures 8 and 9. The double layer capacitance pick at negative potentials is due to the alkali metal amalgam formation on the silver surface, which obviously smoothes out its polycrystalline rough surface, bringing it almost to the geometric value. The double layer capacitance pick at more positive potentials, due to the anodic dissolution of silver, increases its polycrystalline rough surface area.

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