A NEW MODEL OF THE ELECTRIC DOUBLE LAYER AT ELECTRODES IN MOLTEN SALTS

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ABSTRACT

A new model of the electric double layer at electrodes with and without faradic current in molten salts has been developed. As in other solvents, the double layer is assumed to be composed of two layers: the compact layer and the diffuse layer. The compact layer consists of the primary solvation shell, composed of specifically adsorbed anions and/or neutral molecules. For electrodes with faradaic current the charge density of the compact layer is calculated from the charge of the closely packed anions, decreased by the charge neutralized by the faradaic and/or outer current flowing through the interface and the adsorption of neutral molecules. For ideally polarisable electrodes (no faradaic current) the capacitance of the compact layer is the Helmholtz capacitance. The diffuse layer, which extends from the end of the compact layer, is formed by the counterions to the ions adsorbed specifically in the primary solvation shell. The model is tested by the double layer capacitance of the solid silver electrode in the molten AgCl (0.4) + NaCl (0.6) mixture, which was split into compact and diffuse layer capacitances.

INTRODUCTION

There is no general model of the electric double layer on electrodes in molten salts (1). This statement is true not only for electrodes with a faradaic reaction (e.g. AgCl_{molten}/Ag), but also for the polarisable electrodes (e.g. NaCl_{molten}/Pb), without faradaic current. The reason for this may be the fact that most information on any double layer structure is obtained from measurements of the double layer capacitance. The values of the double layer capacitance, however presented in the literature (1-4), are evaluated at different frequencies and amplitude of the ac signal and are thus spread from one to hundreds of \( \mu \text{F/cm}^2 \). These different values are produced by the experimentalist who neglects the dependence of the measured capacitance on frequency.

THEORETICAL

In a previous paper (5) the capacitance of the compact layer of the electric double layer around electrodes in molten salts was evaluated. It has been assumed in this calculation that the compact layer of the electric double layer of metallic electrodes in molten salts is composed of a primary solvation shell, formed by specifically adsorbed...
corresponding halide anions. The capacitance of such a layer was calculated as the Helmholtz type capacitance, with the electric permittivity $\varepsilon$ equal unity

$$C_h = \left( \frac{\partial q}{\partial \phi} \right) = \frac{\varepsilon \varepsilon_0}{d} \quad [1]$$

where $\varepsilon_0$ is the vacuum permittivity and $d$ is the thickness of the compact layer.

The capacitance of the compact layer on the electrode with an exchange current density was calculated by the equation

$$C_{\text{comtl}} = \frac{q_{\text{ps}} - q_{\text{exc}}}{\Delta \phi} \quad [2]$$

where $q_{\text{ps}}$ is the charge density of the primary solvation shell calculated from the closest package of the specifically adsorbed anions, $q_{\text{exc}}$ is the charge density removed from the primary solvation shell by the exchange current density and $\Delta \phi$ is the potential drop in the primary solvation shell.

To calculate the charge density removed from the primary solvation shell by the exchange current density $j_0$, I have to include the inductive model of electric double layer of electrodes with high exchange current density (6,7). The electrochemical behavior of electrodes with high exchange current density is very different from the behavior of typical electrodes having a low exchange current density. Due to the high exchange current density a double layer inductance appears at this electrode interface, which changes the electrode response to both constant current and alternating current perturbation. The impedance spectra of electrodes with high exchange current density are very inductive as most part of the spectrum is placed in the fourth quadrant of the complex impedance plane. The high exchange current density of the reversible electrode is responsible for the appearance of the inductance in the measuring cell.

The literature descriptions (5-7) of the very unusual properties of reversible electrodes immersed in their pure molten salts or concentrated reactant solutions are based on the equivalent circuit approach. In addition to the double layer capacitance, a double layer inductance was introduced into the equivalent circuit, which represents the behavior of such electrode reactions (Figure 1). It is important to see the difference between the capacitance $C$ and inductance $L$ in terms of electronic circuit theory. The most important difference is the phase shift between alternating current and voltage when passing through the capacitance or inductance. The main property of capacitance is that the instantaneous current leads the alternating voltage by $90^\circ$. Contrary to the behavior of a capacitance, the main property of an inductance is that the instantaneous current lags behind the voltage by $90^\circ$. 

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When expressing the properties of the electric double layer in terms of these two circuit elements, it is now much easier to understand the necessity for the existence of both capacitance and inductance. In fact, at each electrode both these elements are present. It is only the magnitude of the effect, exerted upon the behavior of the electrode, which makes it much easier to detect inductance at electrodes with high exchange current density.

Each CRL loop in an equivalent circuit theory has a resonance frequency equal to

$$\omega = \frac{1}{\sqrt{CL}}$$  \[3\]

where the capacitance $C$ and inductance $L$, related to the charge transfer reaction, are obtained from the evaluation of the impedance spectrum of the studied electrode in the corresponding frequency range, where the rate determining step is observed. The reverse of the resonance frequency is the reaction time $\tau$

$$\tau = \sqrt{CL}$$  \[4\]

which can be used to calculate the charge density removed from the primary solvation shell by the exchange current density $j_0$

$$q_{exc} = j_0 \tau$$  \[5\]

The potential drop in the compact layer was evaluated from the Helmholtz capacitance, assuming full coverage of the metallic surface by the specifically adsorbed anions. The value of the capacitance of the compact layer of the electric double layer on liquid metallic electrodes in pure molten salts and their mixtures, in the presence of reversible reactions with large exchange current density, appeared to be very small, of the order of a few $\mu$F-cm$^{-2}$ (5).

As pointed out earlier, each electric double layer is composed of both compact and diffuse layers. The diffuse layer is formed by the charge of the counterions to the ions forming the primary solvation shell. In the alkali halide melts, in which the primary solvation shell is composed of chloride or fluoride ions, the counter ions will be the alkali metal cations. These cations will be placed in the holes created by the melting process in the structure of the molten salt (8-11). The ionic salt, while melting, increases its volume from a few to even 25%. In that way a large number of holes is introduced into the melt structure, which are the possible places for holding the excess charge from the interface. The average volume of such a hole can be calculated from the experimental value of the surface tension $\sigma$ of the melt by equation (11)
In alkali chloride melts the average volume of a hole is roughly twice as large as
the volume occupied by the chloride anion and therefore can easily accommodate an
excess alkali cation, which is smaller than the chloride anion. Such a diffuse layer
subjected to thermal motion will form a space charge, which can create another
capacitance, in series with the capacitance of the compact layer. The potential in the
diffuse layer should drop from the value just outside the IHP (which is not known) to
zero in the bulk of the melt.

THE EVALUATION OF THE DOUBLE LAYER CAPACITANCE FROM THE
EXPERIMENTALLY RECORDED IMPEDANCE SPECTRA

Only an ideally polarisable electrode immersed in an electrolyte without specific
adsorption can be represented by an equivalent circuit, which contains only one
capacitance (the double layer capacitance). All real electrodes, however, have other
capacitances such as reaction capacitance, adsorption or intermediate adsorption
capacitance, capacitance due to chemical homogeneous reactions coupled with the charge
transfer, etc. These capacitances represent certain processes, which occur in a different
time scale and are thus frequency dependent. Many papers that deal with double layer
capacitance measurements by the use of bridge methods, which operate at a one fixed
frequency, evaluate usually one specific capacitance that is a combination of series and/or
parallel capacitances, which are active in the frequency range used. Extreme care must
be thus taken in the measurements and/or evaluation of the double layer capacitance. The
recommended procedure involves measuring of an impedance spectrum in a broad
frequency range and evaluation of all the capacitances present by a suitable equivalent
circuit in a proper frequency range.

In this treatment I shall assume that the experimentally evaluated data from the
analysis of the impedance spectra double layer capacitance is a series combination of the
capacitance of the compact layer (C^coml.) and diffuse layer (C^diff.) as presented in Figure
2.

The double layer capacitance C^dl is thus

\[
C_{dl} = \frac{C_{coml}C_{diff.}}{C_{coml} + C_{diff.}}
\]  

[7]

In the above equation the compact layer capacitance can be calculated from
equation [2] and the double layer capacitance C^dl should be evaluated from the recorded
impedance spectra. The diffuse layer capacitance will be thus
In all our previous papers we have been mainly concerned with the evaluation of the mechanism and kinetics of industrially important electrode processes (13-17). The values of the double layer capacitance, although present in the recorded impedance spectra, and evaluated in the procedure of NLLSFit, were not published, as there was no immediate interest in their values and the values were theoretically difficult to explain.

To check the validity of the present model of the electric double layer for high exchange current electrodes, I will use some of these results, although the vast experimental material on double layer capacitance of electrodes with high exchange current density will be published systematically later. An example of such data (18), recorded for the silver electrode in molten NaCl+AgCl salt mixture, will be used to check the validity of the model.

**THE APPLICATION OF THE MODEL TO THE Ag ELECTRODE IN MOLTEN AgCl (0.4) + NaCl (0.6) MIXTURE**

**The Evaluation of the Experimental Double Layer Capacitance**

Molten AgCl – NaCl binary mixtures behave almost ideally (18,19). The kinetics of the silver electrode reaction in this melt, evaluated by the combination of the galvanostatic relaxation method and the electrochemical impedance spectroscopy, have been published (18). The recorded impedance spectra also contain the double layer capacitance, but its value was not evaluated and hence not published.

A typical impedance spectrum of the solid silver polycrystalline electrode (total true area – roughness factor 2.0 - of two solid Ag electrodes was 0.73 cm²) over the frequency range 10 Hz to 1 MHz, recorded at the equilibrium potential in a two electrode configuration by the use of a Solartron 1260 Phase Gain Analyzer (without a potentiostat) is presented in Figure 3. It is a very typical, inductive impedance spectrum, which was worked out according to the reasoning given above using a typical equivalent circuit of an electrode with a high exchange current density, presented in Figure 1. The non-linear least squares fit (NLLSFit) has been performed by the use of Boucamp’s program (20). The equivalent circuit presented in the Figure 3 contains only one capacitance. As mentioned above, the experimental impedance spectrum may contain several capacitances and only one capacitance will be evaluated, which will be their series and/or parallel combination. Such capacitance, obtained by the NLLSFit of the experimentally recorded impedance spectrum, should be thus frequency dependent. And in fact it is, as shown in the Figure 4 (markers). Each point in the graph presented in Figure 4 represents a result of the NLLSFit by Boucamp’s program in the frequency range from 5 Hz (the lowest frequency recorded) to the given frequency on the graph. It is seen that with increase in the upper frequency, the capacitance decreases. But which of them is the experimental double layer capacitance?
To evaluate the double layer capacitance from such a dependence three procedures can be used. The numerical procedure involves an NLLSFit using a function accessible by the equation

\[ C = a + b/f + c \exp(-d/f) \]  

which represent a combination of a linear and exponential function, where \(a\), \(b\), \(c\) and \(d\) are constants and \(f\) is the frequency (upper value of the frequency range used). The solid line in Figure 4 represents the NLLSFit by equation (9).

The graphical procedure is simpler and involves two linear extrapolations of the high frequency part (1MHz to 300 kHz) and the low frequency part (50 kHz to 5 kHz). The value of the experimental double layer capacitance is obtained as the intersection of the two straight lines and in the case of the analyzed impedance spectrum is 1.98 \(\mu\text{F cm}^{-2}\), whereas the constant \(a\) of equation (8) for the same spectrum is 2.08 \(\mu\text{F cm}^{-2}\).

The above-described procedures, although giving correct values of the double layer capacitance, are somewhat onerous and rather laborious. The same results can be obtained by the application of an extended equivalent circuit to the modeling of the experimental impedance spectrum, which would take into account also the roughness of the solid polycrystalline silver electrode surface. Such an equivalent circuit is presented in the Figure 5, where the CPE stands for the constant phase element (20). The NLLSFit of the recorded impedance spectra with this equivalent circuit over the whole frequency range produces a constant, frequency independent, value of the double layer capacitance. Such values are presented in Table 1.

| Table 1. The double layer capacitance of the solid silver electrode (true area 0.73 cm\(^2\)) in the molten AgCl (0.4) + NaCl (0.6) mixture at several temperatures. |
|----------------------------------|-------------------|
| Temperature \(/{^\circ}\text{C}\) | \(C_{\text{dl}}/\mu\text{F cm}^{-2}\) |
| 730 | 1.99 ± 0.06 |
| 750 | 1.88 ± 0.08 |
| 770 | 1.77 ± 0.21 |
| 790 | 1.65 ± 0.26 |
| 810 | 1.54 ± 0.13 |

The values of the double layer capacitance presented in Table 1 are rather low when compared to some values presented in the literature by authors who have neglected the frequency dependence of this value. As this measured capacitance is a series combination of the value of the compact layer capacitance and the diffuse layer capacitance we have to resolve it into the component capacitances (\(C_{\text{coul}}\) and \(C_{\text{diff}}\)).
The Evaluation of the Compact Layer Capacitance

The compact layer capacitance should be calculated by equation [2] in which the charge density of the primary solvation shell in this chloride melt amounts to

\[ q_{\text{psx}} = \frac{e}{4r^2} = 1.22 \text{ C} \cdot \text{m}^{-2} \]  \[10\]

where \( e \) is the elementary charge and \( r \) is the chloride anion radius. This charge density of the primary solvation shell will have to be corrected for the charge neutralized by the faradaic exchange current density (equation [3]). The exchange current density evaluated earlier by the combination of the galvanostatic relaxation and the electrochemical impedance spectroscopy methods (18,19), recalculated into the true electrode area, is given in Table 2. Also, the reaction time calculated by equation [4], in which the capacitance \( C \) and inductance \( L \) are obtained from the evaluation of the impedance spectrum of the silver electrode, is also presented.

To evaluate the capacitance of the compact layer one needs to know the value of the potential drop across the primary solvation shell. Its value can be calculated from the Helmholtz capacitance (equation [1])

\[ C_H = 1.8854 \cdot 10^{-12} \cdot 1.81 \cdot 10^{-10} \cdot 100 = 4.89 \mu \text{F} \cdot \text{cm}^{-2} \]  \[11\]

assuming that the faradaic current does not change much the structure of the primary solvation shell

\[ \Delta \varphi = \frac{q_{\text{psx}}}{C_H} = \frac{1.22}{0.0489} = 24.95 \text{ V} \]  \[12\]

The potential drop from the metal surface to the middle of the chloride anion is not a measurable quantity and has purely theoretical meaning. The thus calculated capacitance of the compact layer is presented in Table 2. It is seen in Table 2 that the capacitance of the compact layer increases slightly with temperature increase, and this increase may be due to a small increase in the dielectric constant in the IHP, assumed above to have a value of unity.
Table 2. The capacitance of the compact layer of the silver electrode in the molten AgCl (0.4) + NaCl (0.6) mixture at several temperatures.

| Temp. / °C | $j_0 / \text{A cm}^{-2}$ | $\tau / \mu$s | $q_{\text{exc}} / \text{C m}^{-2}$ | $C_{\text{coml}} / \mu\text{F cm}^{-2}$ |
|------------|--------------------------|--------------|-----------------|-----------------|
| 730        | 1.865                    | 26.3         | 0.491           | 2.92            |
| 750        | 1.918                    | 25.0         | 0.481           | 2.96            |
| 770        | 1.972                    | 23.8         | 0.470           | 3.01            |
| 790        | 2.025                    | 22.5         | 0.457           | 3.06            |
| 810        | 2.079                    | 21.3         | 0.443           | 3.11            |

The Evaluation of the Diffuse Layer Capacitance

Once the value of the compact layer capacitance is evaluated from the present model, the capacitance of the diffuse layer can be calculated by equation [7]. The results of such evaluation are presented in Table 3, where all the components of the double layer capacitance of the solid silver electrode at several temperatures are given.

It is seen in Table 3 that the capacitance of the diffuse layer decreases with temperature increase, as a result of increasing the thickness of the diffuse layer upon increasing the temperature.

Table 3. The double layer capacitance and its components of the silver electrode in the molten AgCl (0.4) + NaCl (0.6) mixture at several temperatures.

| Temp. / °C | $C_{\text{di}} / \mu\text{F cm}^{-2}$ | $C_{\text{coml}} / \mu\text{F cm}^{-2}$ | $C_{\text{diff}} / \mu\text{F cm}^{-2}$ |
|------------|-------------------------------------|--------------------------------------|----------------------------------|
| 730        | 1.99 ± 0.06                         | 2.92                                 | 6.26                             |
| 750        | 1.88 ± 0.08                         | 2.96                                 | 5.16                             |
| 770        | 1.77 ± 0.21                         | 3.01                                 | 4.31                             |
| 790        | 1.65 ± 0.26                         | 3.06                                 | 3.62                             |
| 810        | 1.54 ± 0.13                         | 3.11                                 | 3.07                             |

DISCUSSION

The silver electrode used for testing the new model of electric double layer of an electrode with high exchange current density is a solid polycrystalline electrode with a roughness factor equal 2. This means that its true area was twice that of its geometrical area. The impedance measurements recorded on solid polycrystalline electrodes are usually less reproducible than at liquid metallic electrodes. The main reason why this electrode was used for testing was, however, because the charge transfer of the silver electrode is a one step one electron transfer process with no other complications of the electrode process. There is certainly the nucleation overpotential at very low frequencies (below 100 Hz) but that frequency range is not needed in the evaluation of the double layer capacitance.
The evaluated double layer capacitances are rather low. This is due to the fact that the electric permittivity (dielectric constant) of molten salts is relatively low (5 to 10) being of the order of their value for ionic crystals (21). It is very well known from the structure of the electric double layer in aqueous electrolytes (1, 22-25), that the dielectric constant decreases from around 78 in the bulk of the diluted electrolyte to 6 at the OHP and even less at the IHP. Similar behavior has been assumed to exist in the present model of the electric double layer in molten salts, in which the dielectric constant can decrease from a much lower value (around 5-10) to almost unity at the metal surface. In fact, the dielectric constant inside the double layer was found to be 1.3 from an experiment that measured the liquid aluminum drop velocity in an outer electric field in a molten cryolite melt (26).

The capacitance of the compact layer, which is in fact a monolayer of chloride anions, is very little temperature dependent. Such behavior is rather obvious. The main temperature dependence of the double layer capacitance is due to the thermal motion of the sodium cations (counterions), moved inside the holes, which are created in the molten salt structure by the melting process, which create the diffusive capacitance. The increase in temperature should greatly increase the size of the diffuse layer and thus decrease the value of the diffuse capacitance. The theory of the diffuse layer capacitance of electrodes in molten salts will be published separately (27).

REFERENCES

1. R. Parsons, Chem Rev. 90, 813 (1990).
2. A. D. Graves, J. Electroanal. Chem. 25, 349 (1970).
3. D. Inman and D. G. Lovering, Comprehensive Treatise of Electrochemistry, Vol. 7 (B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan, and R. E. White, eds.) Plenum Press, New York, 1983.
4. J. O'M. Bockris and A. K. N. Reddy, Modern Aspects of Electrochemistry, Plenum Press, New York, 1977.
5. A. Kisza, J. Electroanal. Chem. In press.
6. A. Kisza, Polish J. Chem. 67, 885 (1993).
7. A. Kisza, Polish J. Chem. 70, 922 (1996).
8. A. Kisza, Wiadomości Chemiczne, 24, 243 (1970).
9. A. Kisza, Wiadomości Chemiczne, 24, 461 (1970).
10. Molten Salt Chemistry, M. Blander Ed. Interscience, 1964.
11. Fused Salts, B. R. Sundheim, Ed., M. Graw Hill, 1964.
12. A. Kisza, Polish J. Chem., 68, 613 (1994).
13. A. Kisza, J. Kaźmierczak, B. Børresen, G. M. Haarberg and R. Tunold, J. Appl. Electrochem. 25, 940 (1995).
14. A. Kisza, J. Kaźmierczak, B. Børresen, G. M. Haarberg, R. Tunold, J. Electrochem. Soc. 114, 1646 (1997).
15. J. Kaźmierczak, A. Kisza, B. Børresen, G. M. Haarberg and R. Tunold, Proceedings of the Eleventh International Symposium on Molten Salts, JES, Proceedings volume 98-11,114 (1998).
16. J. Kaźmierczak, A. Kisza and R. Tunold, To be published.
17. A. Kisza, J. Thonstad, J. Kaźmierczak, T. Eidet, J. Hives. Molten Salt Chemistry and Technology 5,Trans. Tech. Publ. H. Wendt Ed., 263 (1998).
18. A. Kisza, J. Dzielendziak and J. Kaźmierczak, *Polish J. Chem.* 72, 2321 (1998).
19. J. Dzielendziak, *PhD Thesis*, University of Wroclaw, 1998.
20. B. Boucamp, *Equivalent circuit*, University of Twente, Holland (1988/89).
21. A. Kisza, *J. Chem. Phys.* 47, 2196 (1967).
22. J. O'M. Bockris and S. U. M. Khan, *Surface Electrochemistry. A molecular level approach*. Plenum Press, New York, 1993.
23. Z. Galus, *Fundamentals of Electrochemical Science*, 2nd ed., Ellis Horwood, New York, 1994.
24. P. Delahay, *Double layer and Electrode Kinetics*, Wiley-Interscience, New York, 1965.
25. A. J. Bard, R. L. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, John Wiley, New York, 2001.
26. Y. P. Nikitin, O. A. Esin and V. V Khlynov, *Surface Phenomena in Metallurgical Processes*, Consult Bur., A. I. Belyaev, Editor New York, 1965.
27. A. Kisza. To be published.
Figure 1. The equivalent circuit of an electrode with high exchange current density in a molten salt mixture.

Figure 2. The series combination of the compact and diffuse layers.

Figure 3. An impedance spectrum (Bode plot) of a solid silver electrode in a molten AgCl (0.4)+NaCl (0.6) mixture at 790°C. Markers – experimental values.
Figure 4. The dependence of the experimental capacitance upon the frequency. Markers – experimental values, line – NLLSFit. Temperature 790°C.

Figure 5. The equivalent circuit of a solid polycrystalline electrode with high exchange current density in a molten salt mixture.