

The Double Layer Capacitance of the Liquid Lead Electrode in Molten NaX-KX (X = Cl, Br, I) Eutectic Mixtures

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Using the Electrochemical Impedance Spectroscopy, the double layer capacitance of the liquid lead electrode in the molten NaX-KX eutectic mixture has been evaluated at several temperatures at the rest potential, and in the potential range from 0 to -1 V against reversible lead electrode in the same melt. At no applied potential the liquid lead electrode in the studied eutectic melts can be treated as an “ideally polarizable” electrode. It has been found that the double layer capacitance at the rest potential is very small of the order of $0.9 \mu\text{F cm}^{-2}$ for chloride, 0.6 for bromide and $0.2 \mu\text{F cm}^{-2}$ for iodide melts. As expected its value is decreasing with the increase of the temperature. At the far negative end of the potential range (-1.0 V), the double layer capacitance is decreased by the faradaic process (formation of the alkali metal – amalgam in liquid Pb). With the increase of the potential, the rate of this process decreases and the double layer capacitance increases. With a further increase of the potential, the alkali metal cations in the primary ionic shell are substituted by the halide anions, decreasing the charge density in the primary ionic shell, which results in the decrease of the capacitance toward some small value at the “potential of zero charge”. Still further increase of the potential creates a new double layer, composed mainly of halide ions and the charge density increase is accompanied by the increase of the double layer capacitance. When the anodic dissolution of the metallic lead starts, another decrease of the double layer capacitance is observed. The evaluated values are much lower than the previous results, obtained in early sixties of the 20-th century, which has been obtained by the neglecting of the frequency dependence of the measured capacitance.

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

Most of the measurements of the capacitance of metallic electrodes in molten salts have been performed in early sixties of the 20-th century. In a series of papers Ukshe *et al.* [1–6], using a bridge method operating at 20 kHz, have measured the capacitance of lead electrode in molten alkali halides. The capacitances of the lead electrode, in the form of a tiny lead drop of ~ 0.1 cm² area, were of the order of 20 to $70 \mu\text{F cm}^{-2}$ at several potentials and temperatures. These capacitances, ascribed as the double layer capacitances, were found to be potential dependent in a narrow parabolic shape. The minimum value of the capacitance at some potential (against reversible lead electrode in the same melt) was usually around $20 \mu\text{F cm}^{-2}$ and it has been called double layer capacitance at the potential of zero charge (pzc). There was another, strange, feature of this capacitance – potential dependence. There was a very steep slope of the capacitance increase at both larger positive and/or negative potentials,

which suggests that the capacitance can be unlimited. Also in the work by Inman and Graves [7–9], the measured capacitance was increasing with the increase of the temperature, which, in spite of several attempts [10,11], has never been explained.

Parsons pointed out [12], that these results do not create any convincing model of the electrical double layer (edl) in molten salts. Two important questions in the previous studies have not been answered: why there is so high capacitance at the pzc and why the measured capacitance was increasing with the increase of the temperature?

In this paper we try to reexamine the experimental values of the capacitance of the lead electrode in the alkali NaX-KX molten eutectic mixtures ($X = \text{Cl, Br and I}$) for two reasons: The first reason is the enormous improvement of the experimental ac techniques, which offers the contemporary EIS with both its hardware and software [13,14,15], as compared to the possibilities of ac bridges from the early sixties. In addition, the early investigators have not realized that the measured capacitance is strongly frequency dependent. The second reason is the progress in the understanding of the electrode reactions in molten salts. Namely, it has been shown that to characterize a reversible electrode reaction in molten salts, and in particular the phenomena occurring during charge transfer process inside electric double layer, it is not enough to use the double layer capacitance, but also the double layer inductance [16–23]. It has been shown previously [24], that the experimental values of the correctly evaluated double layer capacitance of electrodes with high exchange current densities are fairly small (of the order of few $\mu\text{F cm}^{-2}$). Its value can be resolved into compact layer capacitance and diffuse layer capacitance. For the details the reader is referred to the original paper [24].

It follows from all previous studies, that the lead electrode in contact with molten alkali halides at high temperatures undergoes a spontaneous dissolution with a formation of small amount of Pb^{2+} cations in the vicinity of the electrode. The measured capacitance can thus contain, in addition to the true double layer capacitance composed of the compact and diffuse layer capacitances, also a charge transfer reaction capacitance. This charge transfer reaction capacitance is much larger than the value of the double layer capacitance and can be observed in a much lower frequency range (usually around $\sim 10 \div 20$ kHz). Contrary to the diffuse layer capacitance, which is in series with the compact layer capacitance, the charge transfer reaction capacitance is in parallel to the double layer capacitance. At a given frequency one always measure a sum of these two capacitances. At still lower frequencies, the capacitance of a chemical preceding reaction is to be expected, which is especially high if complex ions are taking part in the electrode process. Extreme care must be thus paid to the procedure of the evaluation of the double layer capacitance (seen in the high frequency range) from the experimental impedance spectrum.

EXPERIMENTAL

Materials. Metallic lead of spectral purity (BDH, UK) was cleaned with abrasives from the surface oxides layer. The following salts used in experiments: sodium chloride p.a (POCH Gliwice, Poland), sodium bromide p.a. (MERCK, Germany), sodium iodide p.a (POCH Gliwice, Poland), potassium chloride p.a (POCH Gliwice, Poland), potassium bromide p.a (POCH Gliwice, Poland) and potassium iodide 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. In this experiment, two identical lead electrodes were connected in series to the Solartron 1260 Phase Gain Analyser. The measuring vessel, used in this two-electrode experiments, presented in Fig. 1, consisted of an alumina crucible filled with molten eutectic mixture of salts was placed in a quartz tube, closed with the brass lid. Two identical lead electrodes, each of 0.21 cm² of geometric surface area, were placed in quartz tubes closed at the bottom. The holes above a metal layer provided contact with the melt. 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 several temperatures.

The second type of experiments was a typical potentiostatic measurement in a three electrode configuration. In this experiment, which was performed in the three electrode cell presented in Fig. 2, only one lead 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 halide in a sodium – potassium halides eutectic mixture and a layer of lead at the bottom served as the reference electrode.

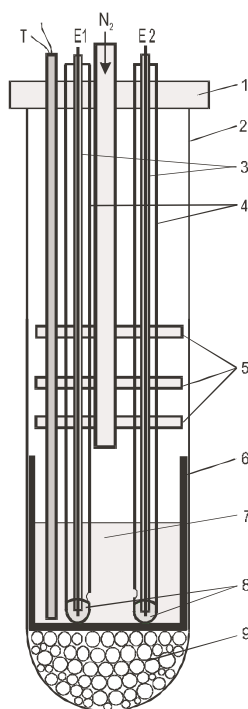


Figure 1. The measuring vessel applied in two-electrode impedance measurements. 1 – brass lid; 2 – quartz tube; 3 – molybdenum wires in alumina insulation; 4 – quartz tubes closed at the bottom; 5 – alumina shields; 6 – alumina crucible; 7 – molten salt; 8 – liquid lead; 9 – ceramic beads; N₂ – nitrogen inlet; T – thermocouple; E1, E2 – identical lead electrodes.

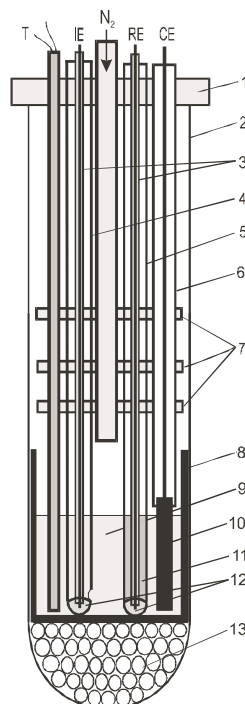


Figure 2. The measuring vessel applied in three-electrode impedance measurements. 1 – brass lid; 2 – quartz tube; 3 – molybdenum wires in alumina insulation; 4 – quartz tube closed at the bottom; 5 – porous alumina tube; 6 – alumina tube; 7 – alumina shields; 8 – alumina crucible; 9 – molten salt; 10 – graphite rod; 11 – lead salt reference solution; 12 – liquid lead; 13 – ceramic beads; N_2 – nitrogen inlet; T – thermocouple; IE – indicator, RE – reference, CE – counter electrodes.

Linear sweep voltammetry was also used to determine the potential range with no faradaic reaction. Impedance spectra were recorded, using the Solartron 1260 Phase Gain Analyser and the Solartron 1287 Interface within the 10 Hz ÷ 100 kHz frequency range at several temperatures. The potential range varied usually from –1 V to 0 V *vs.* the reference electrode with the 50 mV steps. The alternating current amplitude was 10 mV. The indicator electrode was filled with a new portion of lead after finishing measurements in each temperature.

RESULTS AND DISCUSSION

The double layer capacitance of the lead electrode in the molten NaX-KX eutectic mixtures at the rest potential. According to all earlier results, the lead electrode at a rest potential (no applied outer potential), in contact with a molten alkali halide, undergoes some spontaneous dissolution with the formation of an alkali metal amalgam. In this way, one obtains a reversible lead electrode, responding to a tiny concentration of Pb^{2+} cations in its vicinity. Such reversible electrode should in addition to a double layer capacitance, show obviously also certain inductance and diffusion impedance. The impedance spectrum may be thus inductive. In fact the impedance spectrum presented in the Fig. 3, measured in a two electrode configura-

tion (see the experimental procedure), is a typical inductive impedance spectrum, characteristic for a metallic electrode in a diluted solution of its salt.

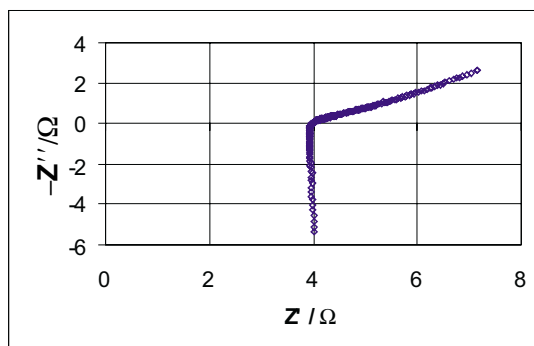


Figure 3. The impedance spectrum of the Pb electrode in molten NaCl-KCl eutectic mixture at 670°C (from 10 Hz to 500 kHz).

The electrode process may be, thus, fairly complex, involving a preceding chemical step followed by two charge transfer steps. One also cannot exclude (to some extent) of the influence of the sodium amalgam electrode reaction. So the equivalent circuit, which should represent the impedance spectrum in the whole frequency range (10 Hz to 500 kHz), may be very complex. To evaluate the double layer capacitance, one needs to use an equivalent circuit, which contain apart from the outer inductance and electrolyte resistance also the double layer capacitance, double layer inductance, high frequency charge transfer step resistance and the Warburg diffusion impedance (Fig. 4).

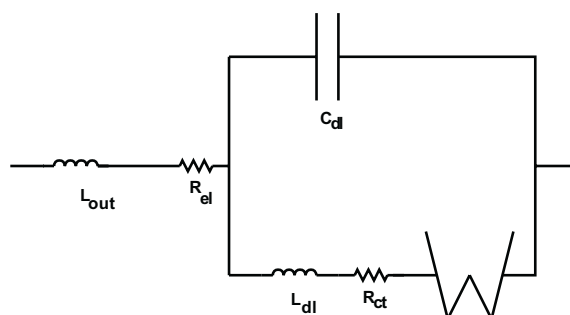


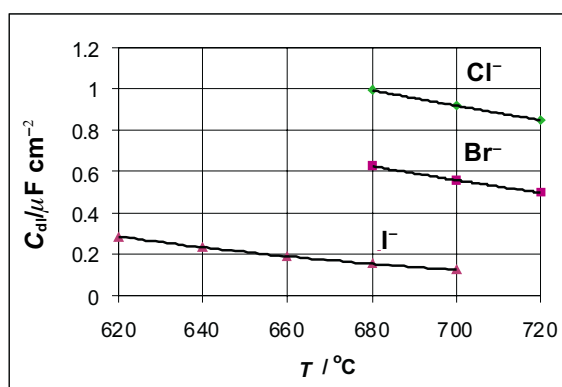
Figure 4. Equivalent circuit of a high exchange current electrode.

It does not represent the impedance spectrum in the whole frequency range (10 Hz to 500 kHz), but it is working well in the high frequency range (10 kHz to 500 kHz). Using this equivalent circuit for the evaluation of the circuit parameters, it is important to remember, that the two elements: double layer capacitance and double layer inductance are not independent variables, as they are related to each other by the resonance frequency [24]. Typical set of parameters of the equivalent circuit used is presented for two temperatures in Table 1.

Table 1. Typical values of the parameters of the equivalent circuit in the molten NaCl-KCl eutectic mixture at several temperatures.

Temperature °C	L_{out} H	R_{et} Ω	C_{dl} F	L_{dl} H	R_{ct} Ω	W $\Omega^{-1} s^{1/2}$
680	$9.17 \cdot 10^{-7}$	3.21	$4.17 \cdot 10^{-7}$	$1.72 \cdot 10^{-7}$	0.74	0.013
700	$9.17 \cdot 10^{-7}$	3.19	$3.86 \cdot 10^{-7}$	$1.77 \cdot 10^{-7}$	0.72	0.014
720	$9.17 \cdot 10^{-7}$	3.15	$3.57 \cdot 10^{-7}$	$1.89 \cdot 10^{-7}$	0.70	0.015

The double layer capacitance of the liquid lead electrode in the molten NaX-KX eutectic mixtures as a function of the temperature (at the rest potential) is presented in Fig. 5.

**Figure 5.** The temperature dependence of the double layer capacitance of the lead electrode (at the rest potential) in the molten NaX-KX eutectic mixtures.

As expected, it is seen in this Figure, that the double layer capacitance is very small, decreases with the increase of the temperature and is also decreasing with the increase of the radius of the halide anion.

The potential dependence of the double layer capacitance of the lead electrode in the molten NaX-KX eutectic mixtures. As described in the experimental section, the potential dependence of the double layer capacitance of the liquid lead electrode in the molten eutectic NaCl-KCl eutectic mixtures was measured in a three electrode cell. After immersion of the working electrode, its rest potential was around -0.03 V against reversible lead electrode in the same melt, which confirms that there is a small concentration of the Pb^{2+} cations (~ 0.5 wt%) in the vicinity of the working lead electrode. The imposition of a constant potential upon the working lead electrode was accompanied by a constant current flow between the working electrode and the auxiliary electrode. This current shown by the current meter of the Solartron 1287 Interface has been changing with the applied potential, as shown for a typical experiment in Fig. 6.

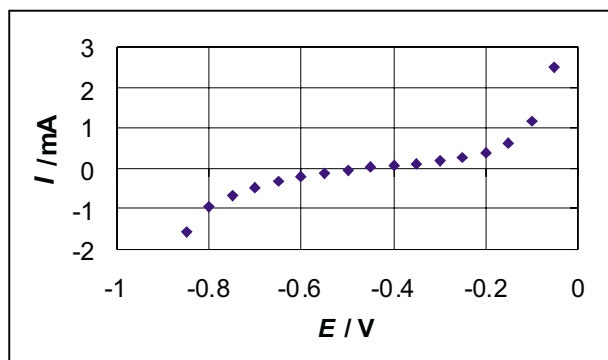


Figure 6. The current between the working (lead) electrode and the auxiliary electrode at different potentials.

At the far negative polarization, the constant current is due to the reduction of the alkali metal cations, while at the positive polarization the constant current is due to the anodic dissolution of the metallic lead electrode. There is a potential range, however, from ~ -0.2 to ~ -0.7 V, in which the current is fairly small (several microamperes) and the liquid lead behaves almost as a polarizable electrode; somewhere in the middle of this potential range (~ -0.5 V) one should expect to find the potential of zero charge. The impedance spectra outside this potential range should be typical for a reversible electrode, while inside this potential range the impedance spectra should be rather capacitive. The impedance spectra in the whole potential range used are presented in Fig. 7.

Indeed, it is seen in Fig. 7, that at the high cathodic polarization ($E = -1.0$ V) and at anodic polarization ($E = 0.0$ V), the impedance spectra show pronounced inductive behaviour, while in the potential range between these extreme values, the impedance spectra exhibit more capacitive features.

While the inductive impedance spectra in the far ends of the cathodic and anodic polarization potential can be modeled by the equivalent circuit presented in Fig. 4 (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 in the potential range of the lead electrode in the whole frequency range from 10 Hz to 100 kHz was only possible by the equivalent circuit presented in Fig. 8, with a constant phase element (CPE) loop.

The traces of the faradaic processes from both positive and negative polarization were seen all over the potential range used and, therefore, the double layer inductance must have been left in the equivalent circuit. 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 rod) 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 represent the auxiliary electrode. The constant phase element loop accounts well for the impedance of the porous graphite electrode.

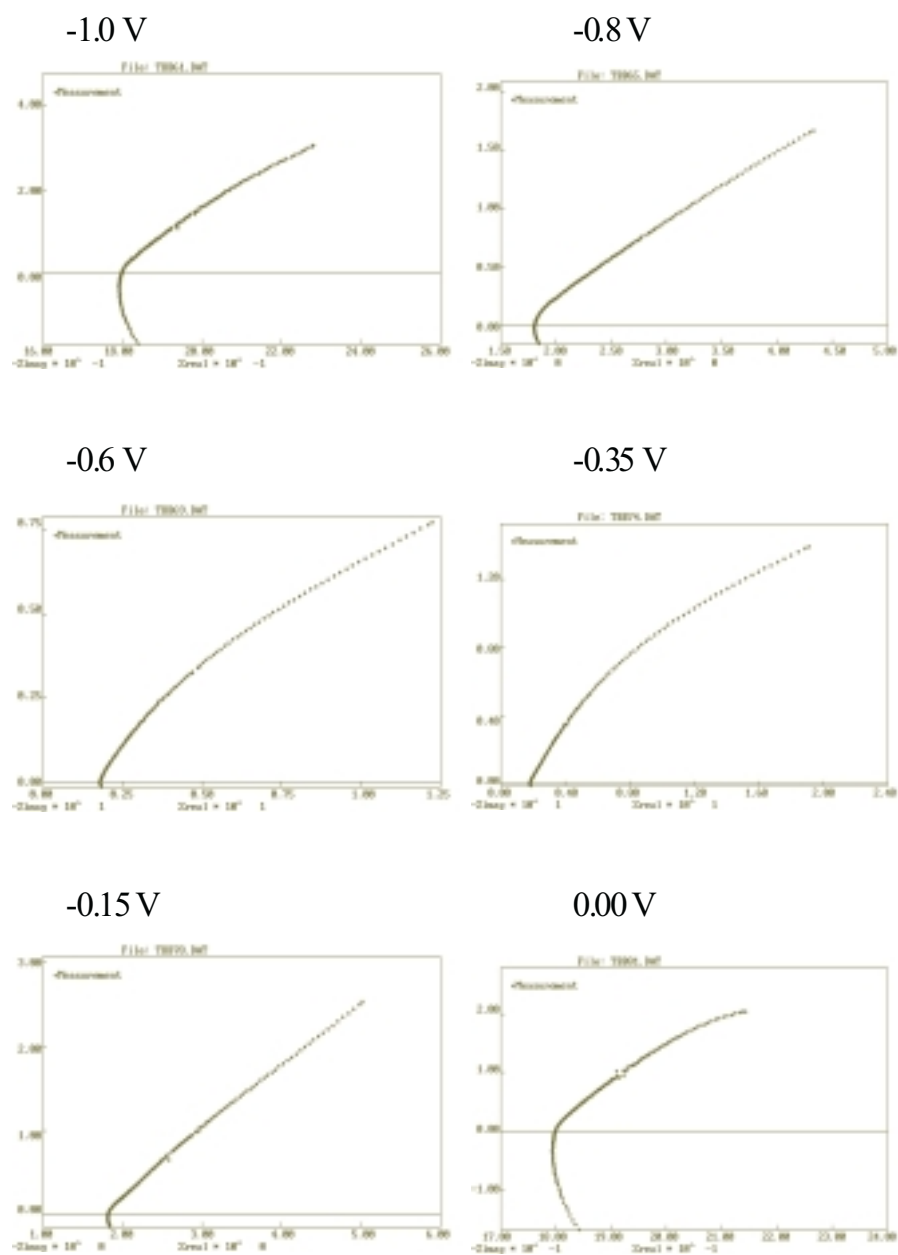


Figure 7. The impedance spectra of the lead electrode in the molten NaBr-KBr eutectic mixture at several potentials.

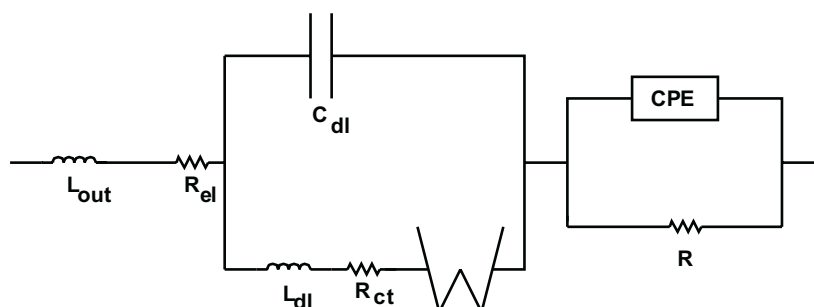


Figure 8. The equivalent circuit used in the potential range around the potential of zero charge.

For the precise evaluation of the double layer capacitance, the equivalent circuit with one capacitance (Fig. 4) was used, but the frequency range used for such modeling was restricted to the high frequency range from 5 kHz to 100 kHz.. The modeling was performed by the Boukamp's program [14] and checked with the Zview program of Macdonald [15]. The agreement was very good in all cases. In that way the capacitance of the lead electrode in the chloride melt was evaluated as a function of potential at three temperatures and is presented in Fig. 9.

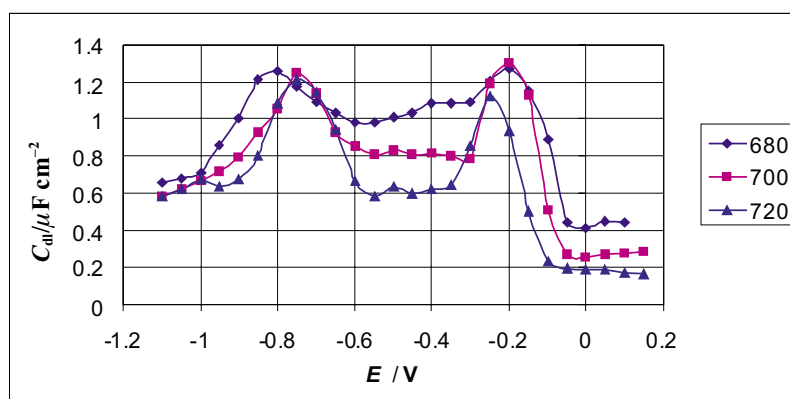


Figure 9. The potential dependence of the capacitance of the lead electrode in the molten NaCl-KCl eutectic mixture at 720°C.

The course of the capacitance with the increase of the potential presented in Fig. 9, represents the state of the electric double layer at a given potential. To explain this dependence more accurately, we present only one curve, at 700°C, in Fig. 10 and mark the characteristic points with letters.

At the far negative potentials (point A in Fig. 10), the reduction of the alkali cations and the formation of alkali metal – lead amalgam occur and the compact layer is mainly composed of the alkali metal cations. As pointed out in the earlier paper [24], each faradaic reaction with the exchange current decreases the compact layer capacitance and also the total double layer capacitance. With the increase of the potential (A→B), this reduction process slows down, the current flowing through the electrode

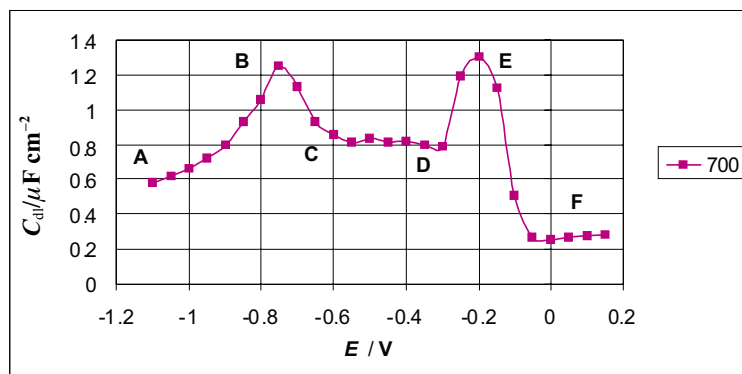


Figure 10. Description in the text.

surface is decreasing (see Fig. 6), which increases both the compact layer and double layer capacitances. At the potential B, the faradaic process ceases and the electrode becomes to some extent polarizable. More chloride anions start to be placed in the primary ionic shell, which decreases the positive charge of the alkali cations and this is accompanied by the decrease of both compact and diffuse layer capacitances (B→C). In the potential range from C to D the double layer capacitance is almost constant and somewhere in the middle of this potential range pzc is situated. Increasing the potential further, the ions present in the primary ionic shell are now overwhelmingly chloride anions, and, therefore, a new edl is created. At the potential E a new electrode (anodic) process starts, which is the lead dissolution. Its rate increases with the increase of the potential, and for the reasons explained above [24], the compact layer capacitance decreases and so is the double layer capacitance. The capacitance corresponding to the end of this decrease is, however, lower (point F), as compared to the level of the capacitance of the far negative end of the potential (point A). This is, however, not surprising, as the two different double layers: at the point A, where the primary ionic shell is composed of alkali cations, and at the point F, where the primary ionic shell is composed of halide anions, differ by their compact layer capacitance. The compact layer capacitance at A amounts, according to the Helmholtz equation [24], to $\sim 8.5 \mu\text{F cm}^{-2}$, while the compact layer capacitance formed at point F amounts to around $4.89 \mu\text{F cm}^{-2}$ (in the chloride melt).

The changes of the double layer capacitance with the temperature are not large, but a decreasing tendency is obvious. Fig. 11 presents the dependence of the double layer capacitance upon potential for different halide anions. As the bromide and iodide anions are larger than the chloride anions, a decrease of the double layer capacitance is expected and such – to the experimental accuracy – are the experimental results presented in Fig. 11.

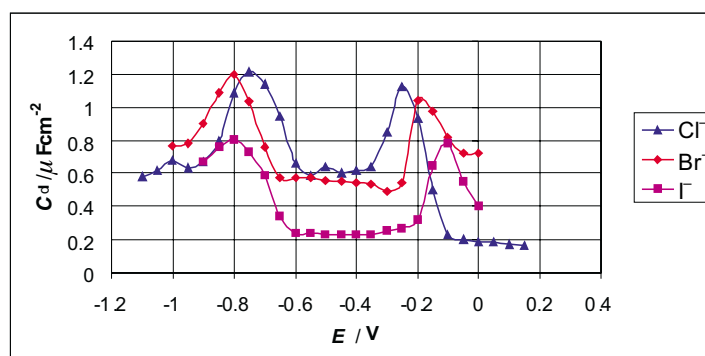


Figure 11. The dependence of the double layer capacitance of the lead electrode at 700°C upon the halide anion.

There is no real dependency of the position of the potential of maximum capacitance at the most negative polarization on the type of halide anion. This is, however, the expected case, as the faradaic process in this potential range is the reduction of the alkali cations and this process is the same in all the eutectic melts studied. The faradaic process at the anodic potentials depends upon the halide anions, and, therefore, the maximum capacitance moves toward more positive potentials from chlorides to iodides.

The interpretation of the results by the inductive model of the electric double layer of electrodes in molten salts. In the previous paper [24] a model of the double layer of electrodes in molten salts was introduced, as a series combination of the compact layer capacitance and the diffuse layer capacitance. The proposed model of the electric double layer of electrodes with high exchange current density allows for the calculation of the compact layer capacitance. It has been assumed in this calculation, that the compact layer of the electric double layer is composed of a primary ionic shell, formed by specifically adsorbed monolayer of chloride anions. The capacitance of such a layer is calculated as the Helmholtz capacitance, with the dielectric permittivity equal to 1

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

where ε is the dielectric permittivity of the molten salt between the parallel plates, ε_0 is the dielectric permittivity of the vacuum and d is the thickness of the compact layer, taken as the radius of the corresponding halide anion. Using this equation the calculated Helmholtz capacitances for the studied halide anions are presented in Table 2.

Table 2. The Helmholtz capacitance of the compact layer with primary ionic shell composed of the halide anions.

Anion	Radius m	C_H $\mu\text{F cm}^{-2}$
Cl^-	$1.81 \cdot 10^{-10}$	4.89
Br^-	$1.95 \cdot 10^{-10}$	4.54
I^-	$2.16 \cdot 10^{-10}$	4.10

This capacitance is then corrected for the exchange current density. The corresponding amount of counterions to the specifically adsorbed anions in the primary ionic shell is transferred to the neighbouring holes, creating the diffuse layer.

The double layer capacitance, evaluated experimentally from the analysis of the impedance spectra, is a series combination of the capacitance of the compact layer (C_{comL}) and diffuse layer capacitance (C_{difL}) the double layer capacitance C_{dl} is, thus

$$\frac{1}{C_{\text{dl}}} = \frac{1}{C_{\text{comL}}} + \frac{1}{C_{\text{difL}}} \quad (2)$$

The capacitance of the diffuse layer is calculated from the experimentally evaluated double layer capacitance, and calculated by the inductive model, compact layer capacitance.

At the rest potential the exchange current density of the studied lead electrode in pure molten alkali NaX-KX eutectic mixture is very small, so we can neglect the current correction and use the Helmholtz capacitance as the compact layer capacitance. The calculated then diffuse layer capacitances are presented in Table 3.

Table 3. The double layer and diffuse layer capacitances of the lead electrode at the rest potential in molten alkali halide eutectic mixtures.

Temperature °C	Cl ⁻ $C_{\text{dl}}/\mu\text{F cm}^{-2}$		Br ⁻ $C_{\text{dl}}/\mu\text{F cm}^{-2}$		I ⁻ $C_{\text{dl}}/\mu\text{F cm}^{-2}$	
680	0.993	1.24	0.627	0.728	0.155	0.161
700	0.919	1.13	0.559	0.638	0.126	0.130
720	0.850	1.03	0.499	0.561	0.103	0.105

The values of the double layer capacitances are, of course, smaller than the corresponding values of the compact layer capacitance, and, as expected, are decreasing with the temperature increase and the size of the halide anions. Although the measured values of the double layer capacitance are fairly small, they are not equal zero at any potential. It may be, thus, necessary to assume, that there is a certain residual capacitance, due to other, not yet discovered factors.

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