A New Model of Electric Double Layer of Electrodes in Molten Salts

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There is no general model of electric double layer of 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 that is presumably the fact that most information of any double layer structure is obtained from the measurements of the double layer capacitance. The values of the double layer capacitance, however presented in the literature [1,2], are evaluated at different frequencies and amplitude of the ac signal and are thus spread from single to hundreds of $\mu F/cm^2$. Such different values of the double layer capacitance are produced by the experimentalist, who neglects the dependence of capacitance on frequency.

In the presented model, similarly to other solvents, the double layer is assumed to be composed of two layers: the Helmholtz compact layer and the diffuse layer. The Helmholtz compact layer consists of the primary solvation shell, composed of adsorbed anions and/or neutral molecules. The diffusive layer is formed by the charge of the counterions to the ions forming the primary solvation shell and extends from the inner Helmholtz plane toward the bulk of the melt. What follows will concern the compact Helmholtz layer only.

The capacitance of the compact layer is calculated by the Helmholtz equation

$$C_{\mathrm{dl}} = \left(\frac{\partial q}{\partial \varphi} \right) = \frac{\varepsilon \varepsilon_0}{d}$$

in which the relative electric permittivity ε is taken as equal 1, ε_0 is the permittivity of vacuum and the thickness of the compact layer d is equal to the radius of anion in the primary solvation shell. The charge density of the compact Helmholtz layer is calculated from the charge of the closely packed anions, decreased by the charge neutralised by the faradaic and/or outer current flowing through the interface and the adsorption of neutral molecules.

In chloride melts the capacitance of the compact Helmholtz layer is

$$C_{\mathrm{H}} = \frac{1 \cdot 8.854 \cdot 10^{-12}}{1.81 \cdot 10^{-10}} \cdot 100 = 4.89\,\mu\mathrm{F} \cdot \mathrm{cm}^{-2}$$

The experimental value of the double layer capacitance evaluated in the high frequency range (10 kHz - 1 MHz) of the liquid magnesium electrode [3] in molten $MgCl_2$ (0.2) + KCl (0.8) at 755°C is 2.78 $\mu F \cdot cm^{-2}$. To calculate the experimental value of the double layer capacitance theoretically, the charge density of the closest packed primary solvation shell

$$q_{\mathrm{pss}} = \frac{e}{4 r_{Cl^-}^2} = 1.22\,\mathrm{C} \cdot \mathrm{m}^{-2}$$

is corrected for the charge removed from this layer by the exchange current density j_o

$$q_{\mathrm{exc}} = j_o \tau = 10510 \cdot 5.29 \cdot 10^{-5} = 0.556\,\mathrm{C} \cdot \mathrm{m}^{-2}$$

where τ is the reaction time obtained from the resonance frequency of the low frequency charge transfer step.

The theoretical double layer capacitance is calculated by the equation

$$C_{\mathrm{calc}} = \frac{q_{pss} - q_{exc}}{\Delta \varphi}$$

in which the potential drop in the inner Helmholtz plane, $\Delta\varphi$, is taken from the Helmholtz capacitance.

The thus obtained theoretical value of the double layer capacitance for the liquid magnesium electrode in the above given melt amounts to 2.66 $\mu F \cdot cm^{-2}$, in fair agreement with the experimental value.

The application of this model [4] to the evaluation of the double layer capacitance of the liquid magnesium, aluminium and solid silver electrodes in several melts will be presented.

References

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