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Mendeleev Commun., 2023, **33**, 726–728

Mendeleev Communications

Structure of the interface between a renewable Sn electrode and propylene carbonate solutions

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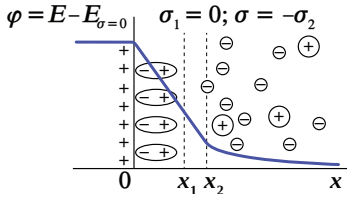
DOI: 10.1016/j.mencom.2023.09.043

The *in situ* electrochemical measurements on a mechanically renewable Sn electrode in propylene carbonate solutions of a surface-inactive electrolyte Bu_4NClO_4 were carried out and their results were analyzed.



Keywords: mechanically renewable Sn electrode, propylene carbonate, Bu_4NClO_4, impedance method, electric double layer.

The adsorption of solvent molecules and ions at charged metal–electrolyte interfaces and the potential distribution in the contact zone affects the kinetics and mechanism of processes at such interfaces. The metal–solution interfaces in non-aqueous solvents are actively explored at the present time. Thus, propylene carbonate (PC) used in this work is assumed to be promising for double-layer supercapacitors due to its wide interval of ideal polarizability (~3 V) in contact with carbon electrodes; moreover, it is used as a component of complex electrolytes in lithium-ion batteries.

There is limited published information about the electric double layer (EDL) structure on electrodes in solutions based on PC and other organic solvents. This is associated with serious experimental complications, in particular, the difficulty of obtaining the reproducible electrode surface.[1] Therefore, such measurements were preferentially carried out on electrodes with an ideally smooth surface, *i.e.* mercury electrodes,[2,3] electrodes of liquid binary alloys based on Ga,[4,5] and polycrystalline Bi electrodes.[6,7] A considerable progress was achieved by carrying out measurements on electrodes which surface was mechanically renewed by cutting a thin (~10 μm) metal layer immediately in the electrolyte solution without breaking the polarization circuit. The design of a special cell equipped with a tool for the renewal of electrodes of certain metals and their alloys is described elsewhere.[8–10]

The mechanical renewal of the electrode surface proved to be efficient for obtaining the electrode surface free of uncontrollable impurities. Using this procedure, we obtained quantitative information about the EDL structure on certain electrodes of metals and alloys of different nature, including Au, Ag, and Al in contact with non-aqueous media,[11,12] and also on Sn electrodes in aqueous and acetonitrile (AN) solutions of surface-inactive electrolytes.[13]

In this work we demonstrate new results obtained from experiments on EDL on the renewed Sn electrode in PC solutions of Bu_4NClO_4 ($TBAClO_4$). Our interest in this system was associated with the fact that Sn is a promising component of thin-film electrodes for lithium-ion batteries.[14,15] On the other hand, we believe that the considered comparison of our new results with the published data allows us to better understand the place of Sn electrodes in the row of mercury-like metals from the viewpoint of their interaction strength with solvent molecules.

The short description of experimental measurements and data processing is given below.†

Figure 1 shows the capacitance–potential (C *vs.* E) dependences (points) measured on the renewed Sn electrode in PC solutions with different concentrations of $TBAClO_4$. These dependences are characterized by a pronounced minimum at $E = -0.39 \pm 0.02$ V with its depth increasing with a solution dilution. As the potential of minimal capacitance is virtually independent on the electrolyte concentration, we can infer the absence of specific adsorption of $TBAClO_4$ on the Sn electrode surface. In other words, $TBAClO_4$ is a surface-inactive electrolyte, and the observed minimum is caused by the maximum EDL diffusivity at the zero-charge potential ($E_{\sigma=0}$).

The capacitance curves shown above were analyzed using the classical EDL model. Using the Parsons–Zobel method, the dependence of C^{-1} on C_D^{-1} was plotted, where C is the experimental capacitance at the potential of its minimum and C_D is the calculated capacitance of diffuse layer at $\sigma = 0$, for different

† The experimental dependences of the electrode impedance components $1/C\omega$ and R (where C is the differential capacitance, $\omega = 2\pi f$ is the angular frequency, f is the ac frequency (Hz) and R is the resistance) on the potential E, and the dependences of the electrode current densities on E (CVA curves) were measured using AUTOLAB PGSTAT 100, with the FRA (Frequency Response Analyzer) system. Details of these measurements are given elsewhere.[9–13]

The traditional treatment and the analysis of impedance diagrams (for f from 100 to 2500 Hz) using the program ZView2®[16] and the CV curves (potential scan rate 100 mV s^{-1}) measured on the periodically renewable Sn electrode in solutions of $TBAClO_4$ in PC allowed us to conclude that the potential interval from −1.85 to 0 V (*vs.* SCE) can be considered as the region of ideal polarization for this system. Therefore, the EDL capacitance in this potential region was measured mostly at the frequency f = 370 Hz which was considered as optimal. Furthermore, it should be noted that in this potential region, the change (decrease) in the measured capacitance values observed during the period from 5 to 60 s after the electrode renewal did not exceed 5%.

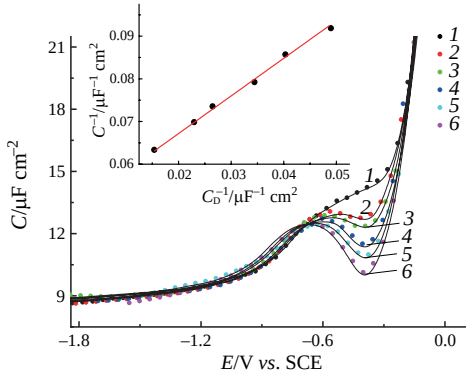


Figure 1 Experimental *C vs. E* dependences (points) on the renewed Sn electrode in PC solutions with different concentrations of $TBAClO_4$: (*1*) 0.1, (*2*) 0.045, (*3*) 0.035, (*4*) 0.02, (*5*) 0.015, and (*6*) 0.01 M; solid lines are the *C vs. E* curves calculated using the Gouy–Chapman–Stern–Grahame model. Inset: the Parsons–Zobel dependence plotted based on the data at the potential of minimal capacitance.

electrolyte concentrations (Figure 1, inset).[17] The PC permittivity was assumed to be 64.4.[1] The slope of the linear dependence is reciprocal to the roughness factor of the surface. It was found to be 1.13. The evident linearity of this dependence allowed us to conclude that this system can be described by the classical Gouy–Chapman–Stern–Grahame phenomenological EDL theory. Moreover, this conclusion is confirmed by the agreement of capacitance curves of the Sn electrode in PC solutions (solid lines in Figure 1) calculated by the Grahame method[18] with experimental dependences for the corresponding $TBAClO_4$ concentrations.

Figure 2 compares the calculated dependences of the inner layer capacitance C_i *vs.* σ for the Sn electrode in PC solutions with the published data for Hg and Ga electrodes in the same solutions.[19] Obviously, similar to AN-based solutions,[13] the C_i values on Ga, Sn, and Hg electrodes are close to one another in PC solutions at the negative surface charges $\sigma < -5$ μC cm^{-2}, and this suggests the identical orientation of solvent molecules in the EDL inner part on these electrodes. As we proceed from $\sigma = -5$ μC cm^{-2} to more positive surface charges, the effect of the metal nature becomes more pronounced. Moreover, C_i values for the Sn electrode, in contrast to Ga, remain sufficiently close to those for the Hg electrode. In other words, the Sn electrode is close to the Hg one regarding its properties.

To assess the lyophilicity of the Sn electrode in contact with PC solutions, we considered the correlation between $E_{\sigma\,=\,0}$ and the work function W_e.[20] Table 1 compares the potential difference between the renewed Sn electrode and the mercury electrode for $\sigma = 0$ and $\sigma = -10$ μC cm^{-2} in PC solutions and the earlier obtained data in AN and aqueous solutions of a surface-inactive electrolyte.[13]

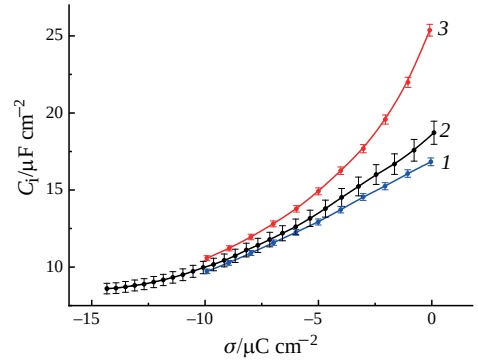


Figure 2 Dependences of the inner layer capacitance C_i on the EDL charge density on different electrodes in PC solutions of surface-inactive electrolyte: (*1*) Hg,[19] (*2*) Sn, and (*3*) Ga.[19]

Table 1 Comparison of the potential difference between Hg and Sn electrodes at zero charges ($\sigma = 0$ μC cm^{-2}) and high negative surface charges ($\sigma = -10$ μC cm^{-2}) in the PC, AN, and aqueous solutions of surface-inactive electrolytes with the work functions of these metals.

Solutions	$\Delta E_{\sigma=0}^{\text{Hg–Sn}}$/V	$\Delta E_{\sigma=-10}^{\text{Hg–Sn}}$/V	$\frac{\Delta W_e^{\text{Hg–Sn}}}{e}$/V
PC solution	0.14	0.11	0.055
AN solution	0.12	0.09	0.055
Aqueous solution	0.2	0.095	0.055

The W_e values used in calculations (4.42 and 4.475 eV for Sn and Hg, respectively) were taken as published.[21]

According to the theoretical concepts suggested by A. N. Frumkin,[20,22,23] the relationship between $\Delta E_{\sigma=0}^{\text{Hg–M}}$ and work function $\Delta W_e^{\text{Hg–M}}$ is as follows:

$$\Delta E_{\sigma=0}^{\text{Hg–M}} = (\Delta W_e^{\text{Hg–M}})/e - \Delta\chi^{\text{S(Hg–M)}} + \Delta(\delta\chi^{\text{Hg–M}}),$$

where $\Delta\chi^{\text{S(Hg–M)}}$ is the difference between the surface potential drops caused by adsorption of solvent molecules on Hg and metal M, and $\Delta(\delta\chi^{\text{Hg–M}})$ is the difference of surface potential drops formed in the metal phases of Hg and M. The negative shift of the metal surface charge results in weakening of the chemisorption interaction with solvent dipoles. At high negative charges, the EDL field favors the orientation of solvent dipoles with their positive end to metal. This should result in the virtual absence of the effect of the nature of metal on the potential drops in the dipole and metal plates of EDL.

As follows from Table 1, the quantities $\Delta E_{\sigma=-10}^{\text{Hg–Sn}}$ calculated based on the results in PC, AN, and aqueous solutions are much closer to $\Delta W_e^{\text{Hg–Sn}}/e$ than the potential differences $\Delta E_{\sigma=0}^{\text{Hg–Sn}}$. Hence, the specific interaction of the Sn electrode with molecules of these solvents is weak at the negative charges. At the potentials close to $E_{\sigma\,=\,0}$, the quantities $\Delta E_{\sigma=0}^{\text{Hg–Sn}}$ increase in the series: AN < PC < H_2O. This allows us to conclude that the chemisorption interaction of Sn with solvent dipoles increases in the same series: AN < PC < H_2O. Hence, at $\sigma \geqslant 0$, the bonding between tin surface and oxygen atoms in molecules of water and PC is stronger than that with nitrogen atoms in AN molecules.

The obtained data allow us to conclude that the Sn electrode is characterized by a very weak (close to the Hg electrode) interaction with PC molecules in a wide potential region. From the practical viewpoint, this result can be interesting and helpful for the development of Li- and/or Na-ion batteries.

This work was supported by the M. V. Lomonosov Moscow State University Program of Development, program no. AAAA-A21-121011590088-4.

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Received: 31st March 2023; Com. 23/7137