Electrosorption-induced deformation of a porous electrode with non-convex pore geometry in electrolyte solutions: A theoretical study

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Abstract – Porous carbon is well known as a good candidate for the development of electrochemical double-layer capacitors. Predominantly, many conventional carbons are microporous and often well described by the assumption of slit pore geometry. However, there is a class of carbons that is significantly different from the others, namely templated mesoporous carbons. In this work, we study electrosorption-induced deformation in CMK-3-like mesopores having non-convex geometry. Our mean-field approach is based on the modified Poisson-Boltzmann equation taking into account the excluded volume of the ions within the hard-sphere model. We assume that the deformation is caused by two effects: ion osmotic pressure and electrostatic interactions of the electric double layers on charged rods. We estimated the pore-load modulus of the CMK-3-like material and found an agreement with the previously obtained values by small-angle neutron scattering (SANS) data analysis. Additionally, we studied the differential capacitance in the non-convex pore geometry and found that the behavior of the differential capacitance profiles was similar to that of the profiles obtained for flat electric double layers: the crowding regime at rather high electric potentials and more pronounced profile asymmetry with increasing differences in the ionic sizes.

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Introduction. – Porous carbon is well known as a good candidate for the development of electric double layer (EDL) capacitors. More precisely, it was chosen due to its large specific surface area, electrochemical stability, and conductivity [1]. The storage mechanism is similar to classical physisorption, i.e., the charge is stored on the electrode/electrolyte interface. Of course, these are not the only similarities and particularly both adsorption [2,3] and electrosorption [4,5] are accompanied by the host material deformation. Thus, an application involving a large number of charging/discharging cycles may cause degradation of the porous electrode and potentially capacitor failure due to the repeating deformations. However, these strains are not always undesirable and can be used, for instance, in the designing of voltage-driven actuators [6]. Though electrosorption-induced deformation is a long-known phenomenon, its mechanism is not fully understood and depends not only on the electrolyte and solvent but also on the adsorbent. So, for example, the variation of pore size distribution or magnitude of surface area can affect the resulting deformation. In this context, CMK-3 templated carbon [7] or monolithic templated carbon with a similar mesoporosity structure [8] are a very interesting example due to a peculiar structure and pore geometry. Both of them have non-convex pores formed by the voids between hexagonally packed carbon cylindrical rods, and, thus, differ a lot from typical carbons.

In ref. [9] the electrosorption-induced deformation of carbon-based supercapacitor electrodes with CMK-3-like mesoporosity was measured by means of in situ small-angle X-ray scattering. The obtained strains were positive and asymmetric, demonstrating higher values at negative voltages. The authors [9] proposed a deformation
mechanism consisting of two major contributions: ion osmotic pressure and C-C bond length variation due to the electron/hole doping during the electrode charging. The interest in these particular measurements is warmed up by the existence of experimentally measured adsorption-induced deformation in similar materials [10] and estimated pore-load moduli. Thus, the existence of a correct electroosorption model would allow cross-checking the pore-load moduli and possibly shed some light on the deformation mechanism of other materials with similar pore geometry.

The adsorption-induced deformation of the CMK-3–like material has been already theoretically studied by two of us [11]. We assumed that each rod was connected with the nearest neighbors by virtual springs. The deformation was considered solely to originate from the change in the inter-rod distances neglecting possible contributions from the rod’s microporosity. In the present letter, we use the proposed model [11] of a CMK-3–like material to describe the electroosorption-induced deformation. We utilize the modified Poisson-Boltzmann equation with the corresponding stress tensor [12] to calculate the distribution of the resultant deformation forces acting on the carbon rods. This may allow us to check the previously proposed deformation mechanism and estimate the pore-load modulus by classical mean-field theory.

Model. – The system geometry aiming to describe electrolyte-mediated rod–rod interactions in CMK-3–like material is presented in fig. 1. It consists of seven non-porous rods of a certain radius, $R$, placed in the centers of hexagonal tiling. The free space between the rods is filled with a 1:1 aqueous electrolyte solution. As CMK-3 is an inverse replica of SBA-15, the rods are interconnected via thin carbon bridges, which are not taken into account explicitly in the model. However, their extension is one of the possible sources of mesoporous adsorption/electroosorption-induced deformation observed in such types of materials [9,10]. We assume that each rod is connected with the nearest neighbors by virtual springs with the elastic constant $\kappa$. The springs are distributed along the rod axis with the density $\rho_{spr}$. This implies that we use Hooke’s law in our model, which is a common assumption for a small strains [2,3,14]. Respectively, we use the assumption that the rigidity of the spring is high enough to prevent a strong elastic response. Therefore, we may split the problem into two parts: the first one, calculation of the forces acting on each rod, and the second one, calculation of the elastic deformation of the system. Thus, the previously proposed model of CMK-3 deformation [11] is utilized in the current study. The total deformation force acting on each rod is a sum of two contributions: electrostatic and steric. The latter is the osmotic pressure of the mobile ions and the former

\[ \varepsilon \nabla^2 \psi = -q(c_+ - c_-), \]

where $\varepsilon$ is the dielectric permittivity of the solution, $q$ is the charge magnitude, $\psi$ is the local electrostatic potential defined with respect to the bulk of the electrolyte (which is assumed zero) and $c_\pm$ are the number densities (concentrations) of the mobile ions in the solution; $\mu_{id} = k_B T \ln (c_\pm \Lambda^2)$ and $\mu_{hs}$ are the ideal and hard-spherical parts of the total chemical potential ($\Lambda$ is the de Broglie thermal wavelengths of the ions), $\mu_0$ is the total chemical potentials in the bulk solution. The excess part of the chemical potential was derived from the bulk limit of fundamental measure theory (FMT) [20,21], which is consistent with the Perkusz-Yevick (PY) approximation in the one-component case (the exact expressions can be

\[ \mu_{id} = k_B T \ln (c_\pm \Lambda^2), \]

\[ \mu_{hs} = \mu_0 (c_\pm \Lambda^2), \]

\[ \psi = \frac{1}{\varepsilon} \ln \left( \frac{c_+}{c_-} \right). \]

Note that a similar physical picture realizes for hexagonally symmetric arrays of linear polymers, such as DNA, e.g., under osmotic stress (see ref. [13] and references therein).
found elsewhere, for instance [12,21])

\[ F = \int_S \sigma \cdot n dS, \]

where \( n \) is the normal to the integration surface (which is a cylinder in our case) and the stress tensor is [12,18]

\[ \sigma = \varepsilon \nabla \psi \otimes \nabla \psi - \left[ P(c_+ + c_- + T) + \frac{\varepsilon (\nabla \psi)^2}{2} \right] I, \]

where \( P(c_+ + c_- + T) \) is the osmotic pressure of the ions in FMT [20,21] approximation and consistent with the chosen expression of chemical potential, \( \varepsilon \) is water dielectric permittivity (which was fixed to 78\( \varepsilon_0 \), where \( \varepsilon_0 \) is vacuum dielectric permittivity) and \( I \) is the unit second-order tensor. The corresponding volume density force has the following form:

\[ f = -\nabla P(c_+ + c_- + T) - q(c_+ - c_-)\nabla \psi, \]

which leads to the standard condition of mechanical equilibrium \( \nabla P(c_+ + c_- + T) = -q(c_+ - c_-)\nabla \psi \) [24], because the tensor is divergence free [18]. Since each integration surface has cylindrical geometry, we can write down the force projections on the \( x/y \)-axis in the following way:

\[ F_x = LR_c \int_0^{2\pi} d\varphi \left\{ -\left[ P + \frac{\varepsilon E_x^2}{2} \right] \cos \varphi \right. \]

\[ + \left. \varepsilon E_x (E_x \cos \varphi + E_y \sin \varphi) \right\}, \]

and

\[ F_y = LR_c \int_0^{2\pi} d\varphi \left\{ -\left[ P + \frac{\varepsilon E_y^2}{2} \right] \sin \varphi \right. \]

\[ + \left. \varepsilon E_y (E_x \cos \varphi + E_y \sin \varphi) \right\}, \]

where \( R_c \) is the radius of an integration contour around the sole carbon rode and \( E \) is the electric field at a certain point with its components \( (E_x, E_y) \). The integration surface does not necessarily coincide with the geometrical cylinder surface because the tensor is divergence free. However, it must always include only one rod. In case when the integration is made precisely over the rod surface the osmotic pressure does not contribute to the force and can be omitted in eqs. (5) and (6).

It was shown that CMK-3-like material adsorption-induced strain also follows the logarithmic dependence on relative pressure at small under-saturation in the bulk vapor phase [10,11],

\[ \varepsilon = \frac{1}{M} (P_{v,0} - P_v + k_B T \rho \ln(P_v/P_{v,0})), \]

where \( M \) is the pore-load modulus equal to \( M = \sqrt{3} \rho_{spr} \kappa \), \( \rho \) is the density of bulk liquid at coexistence, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( P_v \) is the vapor pressure during an adsorption experiment and \( P_{v,0} \) is the saturated vapor pressure. Using the deformation mechanism, which was described above, we can express the electrosorption-induced strain via the forces acting on the rods and pore-load modulus:

\[ \varepsilon_{el} = \frac{\sqrt{3} f_{el}}{2dM}, \]

where \( f_{el} \) and \( \varepsilon_{el} \) are the length density of the deformation force and the corresponding deformation, respectively, and \( d \) is the inter-rod distance. Equation (8) is derived based on the idea of mechanical equilibrium, i.e., the total deformation force acting on the rod must be equal to the total elastic force of the virtual springs. Also, we used the assumption that the deformation-causing force is fixed and defined at the non-deformed pore geometry. Thus, using this equation, we can estimate the consistency of both models.

**Results and discussion.** – We solved the system of equations (1) for three different rod diameters, namely 6 nm, 6.5 nm and 7 nm. These values were reported in ref. [9] along with the interrod distance \( d \approx 9.6 \text{ nm} \). Figure 3 demonstrates the anion and cation density distributions for the aqueous LiCl electrolyte solution. The calculations were performed at the fixed carbon electric potential \( V_c = 0.6 \text{ V} \). There was a positive excess of anions and a negative excess of cations in the vicinity of the rods due to the positive carbon electric potential. The case of 6.5 nm rod diameter is the boundary between the two
regimes obtained: without (figs. 2(a) and (d)) and with (figs. 2(e) and (f)) pronounced EDL overlapping. The first regime is also similar to the ion distributions at lower carbon electric potentials and differs mostly by the EDL width. The second regime is only observed at high carbon electric potentials and is characterized by almost total depletion of cations from the interior space.

We fit the experimentally measured strain curves [9] with eq. (8) using the pore-load modulus as a free parameter. The calculations were performed for the three chosen rod diameters and the results are summarized in table 1. In the case of LiCl aqueous solution we obtain highly non-symmetric force, see fig. 3(a). This is in disagreement with the experimental data and leads to the discrepancy between the obtained elastic moduli (see table 1). The ion specificity is taken into account only via different effective hydrated diameters of the ions [28] (0.764 nm for Li, 0.658 nm for Cs and 0.664 nm for Cl) and, thus, leads to different shapes of the theoretical strain-potential results. However, the magnitudes of the obtained pore-load moduli for 6 nm and 6.5 nm are in range with the previously reported ones [10] obtained for a similar materials by analysing the adsorption-induced strain isotherms (measured by SANS) (0.32–2.36 GPa). The spread of the values is due to different activation times, and it can be attributed to the stiffening of the interconnections between carbon rods [10]. The value 0.32 GPa corresponds to the non-activated sample and apparently can be used as a reference value because the synthesis procedure described in ref. [10] is similar to the one from ref. [9]. Thus, we can conclude that the model can provide realistic pore-load modulus values with the inter-rod distances about 6 nm. We want to stress that our calculations were done without asymmetric deformation contribution, which can in principle change our results and lead to another estimation of inter-rod distance. However, it is obvious from table 1 that the small variation of $R$ (about 0.25 nm) results in a change of pore-load modulus about one decade. Thus the asymmetric part of the strain cannot significantly modify our predictions.

Another interesting comment can be given about the additivity of the inter-rod interactions. We performed additional calculations for similar systems but consisting only of two carbon rods immersed in the LiCl/CsCl aqueous solutions. The obtained force magnitude ($f_0$) was used to predict the generated total electrostatic force in
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Fig. 3: Experimental [9] and theoretical electrosorption-induced strains for both LiCl and CsCl aqueous solutions. The modeling results correspond to the rod diameter equal to 6.5 nm. The comparison is made with the MC sample from ref. [9].

the seven-rod system (see fig. 1). We assumed that the total resultant force is a vector sum of the forces generated by the nearest neighbor rods only. Thus, the direction of the resultant force is radial from the central rod and has an absolute value equal to $2f_0$. The comparison between the additive estimated force and the one obtained for the whole seven-rod system for the case of the 6.5 nm rod diameter is given in the Supplementary Material (SM), see fig. S1(a). The results agree quite well with each other and, thus, at least to some extent, the additive method can be used in this system for force estimations. It can be used to predict on the deformation for a bigger system, for example, for the one shown in fig. S1(b) in the SM. The symmetry allows us to conclude that the strain-generating force is applied only to the “surface” rods. Based on our pair additive assumption, on each “surface” rod several pairs of collinear and oppositely directed forces (electrostatic and elastic) act, that must compensate for each other at the mechanical equilibrium. The same hexagonally ordered system of rods with equally elongated virtual springs would be a solution if the strain satisfies the following condition: $\varepsilon_{el} = \sqrt{3}f_0/dM$. The latter is also eq. (8) for the seven-rod system with pair-wise approximation. Thus, we believe that strain estimation based on seven-rod geometry can reproduce the behavior of a bigger hexagonally ordered system of carbon rods.

It is also instructive to study the differential capacitance ($C$) within the current model. The surface charge density is defined as the total charge on the carbon rods divided by their surface area. We performed calculations for both solutions with a fixed rod diameter, namely 6.5 nm. The differential capacitance profiles have a bell shape [25] form, figs. 4 and S2 in the SM and the magnitudes typical of the models of this type [29]. The latter usually highly overestimate the real experimental values. To make the differential capacitance values more realistic, it is necessary to take into account the short-range specific interactions [30,31] and ionic correlations [32]. Additionally, the differential capacitance in the CMK-3–like system demonstrates the existence of the crowding regime (the differential capacitance is inversely proportional to the square root of the electric potential) [25,29,33] at sufficiently high electric potentials $\approx \pm 0.5$ V. As in the case of a flat EDL [34], the ionic size asymmetry effect makes the differential capacitance slightly asymmetric, the latter is obviously more pronounced for the LiCl case.

Our calculations were performed assuming that the electrode is completely immersed in the electrolyte solution and can deform freely. The latter, however, may not always be fulfilled and an additional constraint can be, for instance, imposed by a solid casing around the electrode. That could lead to competition between the casing and electrode deformation, and thus, the total response will be defined by the elastic constants of both. Even in the case of an absolutely non-deformable shell, the arising forces could lead to structural changes in the electrode.

Finally, we want to comment on some major assumptions and limitations of this work. We neglected the effect of solvent perturbations due to the existence of mobile ions in the solution. This may significantly affect the ions distribution (and other properties, such as electrical potential, dielectric permittivity, etc.) mostly at high packing fractions, i.e., near the electrode surface at sufficiently high electric potentials. Additionally, other effects, such as ion-electrode/ion-ion specific interactions could change the obtained results. Thus, the more general and detailed model is of interest, which should account for the specificity of the theoretical description. We believe that the concept of a modified Poisson-Boltzmann equation can be one of the possible solutions. For example, the solvent can be taken into account as a “full participant” of the
inverse square root of the electric potential absolute value. Incorrect account for steric interactions in microporous, the model and experiment. However, they do not fix the heterogeneity reduce the ordering effects bringing together ions/solvent layering may happen. Carbon roughness and \( \varepsilon_{\text{permittivity}} \) [31].

Equations alongside the concentration-dependent dielectric permittivity [31].

The present model is a local one and, thus, has a limiting applicability in the strong confinement, where the ions/solvent layering may happen. Carbon roughness and heterogeneity reduce the ordering effects bringing together the model and experiment. However, they do not fix the incorrect account for steric interactions in microporous, where interesting effects could happen [35]. This, in general, can be overcome within the framework of classical density functional theory.

An additional factor influencing the result can be the difference in the reference points for an electrode potential definition. The electric potential in the model is defined with respect to the value in the bulk electrolyte, which was taken as zero. The experimental data were obtained with respect to the carbon reference electrode [9]. Ideally, both data sets should be brought to one electric potential scale. However, the moderate shifts should be not dramatic due to almost negligible strain in the interval \(-0.2\)–\(0.2\) V.

Despite, all these limitations we believe that our minimalistic model can provide qualitatively and probably even quantitative insights to the electrosorption-induced deformation of carbon electrodes.

Concluding remarks. – In conclusion, we would like to summarize the main results of our work. Within the simple mean-field model we estimated the inter-rod force generated in a CMK-3-like structure caused by ion osmotic pressure and electrostatic interactions. Using the previously published information about the material structure [9] we estimated the pore-load modulus based on electrosorption experimental data and found an agreement with the data obtained for the similar material by conventional adsorption measurements. Thus, the calculated force magnitude has a realistic order indicating the potential of our electrosorption-induced deformation model (and confirming the discussions of the deformation mechanism in ref. [9]). Additionally, it may indicate that the previously suggested [11] material deformation mechanism is reasonable. We demonstrated that the resulting force acting on each carbon rod can be approximated on an additive (pair-wise) basis, which can be used further to upscale the model to describe the macroscopic sample deformation. Finally, we studied the differential capacitance in the same pore geometry and demonstrated the crowding regime at sufficiently high applied electric potentials. We believe that our results can be useful for the interpretation of electrosorption/adsorption-induced deformation data for CMK-3-like materials as well as for others with non-convex pore geometry.

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Data availability statement: The data that support the findings of this study are available upon reasonable request from the authors.

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