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Langmuir adsorption processes and ions transport under bias potential in capacitive deionisation cells

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Abstract

The electric response of a capacitive deionisation cell submitted to a periodic external electric field is investigated. The case in which the applied potential has a nonzero average value on one period (polarised cell) is considered. The theoretical analysis of the experimental data, relevant to nearly symmetric electrodes, is done in the framework of the Poisson-Nernst-Planck model. The current densities on the electrodes are described by kinetic equations related to the adsorption phenomenon in the presence of a bias potential. We propose a new form for the Langmuir isotherm in which the effective adsorption coefficients depend on the bias potential according to the Boltzmann statistics. This kinetic equation extends the Butler-Volmer equation for non-blocking electrodes also to the blocking ones. The equation proposed here is such that for dc external voltage the total current across the electrodes vanishes.

Keywords: Capacitive deionisation, Electrical impedance,

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Poisson-Nernst-Planck model, Adsorption model

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1. Introduction

The rapid population growth, climate change and the intense exploitation of water for domestic, industrial or agricultural uses are leading to a substantial reduction in fresh water resources in many countries around the world. Since the ocean makes up 70 % of the Earth's surface and accounts for nearly 96 % of the water on the planet, desalination of salty water has become an important alternative source of clean water [1, 2].

Among the different existing desalination technologies, capacitive deionisation is emerging as a promising candidate since it can overcome many of the actual limitations of the most common processes (reverse osmosis, flash distillation and electrodialysis) such as the excessive energy consumption, intensive cost, high salinity residual, and secondary chemical wastes [3].

Indeed, capacitive deionisation is an energy-efficient desalination process because it operates at a low electrode potential (about 1 V) at which no electrolysis reactions occur and without need of chemical reagent during the operation. The working mechanism is quite simple and relies on the removal of ions from aqueous solutions by electrosorption. During the adsorption step, a potential is applied between two highly porous carbon electrodes: cations are adsorbed into the negatively polarised electrode while anions are adsorbed into the positively polarised electrode resulting in two electric double layers at the solid/liquid interfaces. When the potential is removed in the desorption step the adsorbed ions are quickly released back to the bulk electrolyte solution. In the capacitive deionisation process ions transport and adsorption play a fundamental role in the device performance [4].

Thus, the theoretical description of the role of these electrodes has to take into account the bulk behaviour of the charge carriers in the layers close to them as well as the adsorption-desorption mechanisms occurring at their interface with the saline solution [5, 6, 7, 8]. This is the main goal of the present paper, in which a new mechanism for the adsorption on the equivalent electrodes is proposed, in connection with a generalisation of a diffusion model to describe the electric response of a cell to an external excitation.

The paper is organised as follows. In Sec. 2, the fabrication of the cell used in the experiments is described, and the experimental set up used to investigate the electric response of the cell to a periodic external excitation is presented. In Sec. 3, a generalised version of Poisson-Nernst-Planck model for cells limited by different electrodes, taking into account the difference of the diffusion coefficients of the positive from the negative ions, is proposed. A model for the adsorption of ions, in the presence of an external electric field, is developed, assuming that the bulk density of ions just in front of the adsorbing electrode depends on the external electric potential according to the Boltzmann statistics. A cut-off on the potential is introduced to take into account that the range of the surface forces is finite. A detailed comparison of the theoretical predictions of our model with the experimental data is reported in Sec. 4. The conclusions are reported in Sec. 5.

2. Experimental

The cell is a homemade model, composed by two electrodes and an aqueous electrolyte, hosted in a glass beaker. A sketch of the cell is reported in Fig. 1. The electrodes are made of a metallic current collector (titanium, 0.2 mm thickness, GoodFellow), coated with a carbon-based active material. Each electrode is a rectangular slab, with a region of approximately $1.21\,\mathrm{cm}^2$ of active material. The two electrodes are placed inside the cell facing each other, at a fixed distance of 5.5 mm. To ensure reproducibility, the weight of the active material was always checked to be (5.0 ± 0.1) mg. The electrolyte employed is a solution of NaCl 1 M in deionised water (MilliQ, $18.2\,\mathrm{M}\Omega\,\mathrm{cm}$). This concentration of the electrolyte is two orders of magnitude higher compared to common solutions employed in desalination experiments [9]. The purpose is to provide the necessary amount of ions so that the fraction of adsorbed ions leaves almost

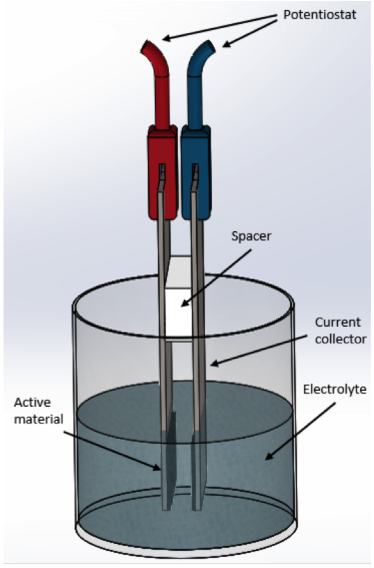

Figure 1: Scheme of the experimental setup.

unchanged the concentration of ions in the bulk, as described in Sec. 3.

The electrodes are prepared as follow. Activated carbon ($1666\,\mathrm{m}^2/\mathrm{g}$, MTI Corporation) is mixed with a polymeric binder (polyvinylidene fluoride, Sigma Aldrich) in weight ratio of 90% and 10%, respectively. Dimethyl sulfoxide (99.5% purity, Sigma Aldrich) is used as solvent. The slurry obtained in this way is sonicated and then stirred overnight to achieve a good homogeneity. The active material is then coated over the current collector by a doctor blade method. The electrodes are dried on a hot plate at 50°C for 15 min. Before starting the electrochemical characterisations, the electrodes are immersed in the electrolyte solution in open circuit condition for 1 hour. Cyclic voltammetry is the electrochemical method employed to study the adsorption-desorption phenomena. This technique relies on applying a periodic potential to the cell, while measuring the current. Further details are provided in Sec. 3.

The electrochemical measurements have been performed with VMP3 potentiostat manufactured by Bio-Logique. This instrument offers potentials range of $\pm 10\,\mathrm{V}$, a maximum current of $400\,\mathrm{mA}$, with a resolution of $5\,\mu\mathrm{V}$ and $760\,\mathrm{pA}$.

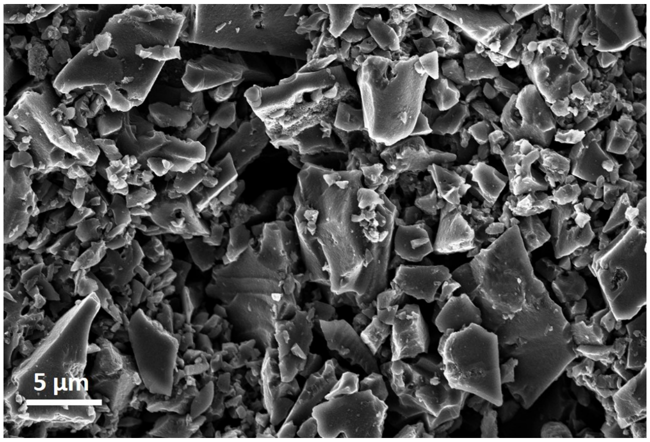

Figure 2: FESEM image of the activated carbon-based electrode.

The accuracy is declared to be $< 0.1\,\%$ of the full scale range. The electrometer has input impedance greater than $1\,\mathrm{T}\Omega$, a capacitance of less than $20\,\mathrm{pF}$ and a bias current lower than $5\,\mathrm{pA}$. Electron microscopy characterisation was carried out with a Field-Emission Scanning Electron Microscope (FESEM Supra 40, manufactured by Zeiss) (see Fig. 2).

3. Modelling

In this section, we shall give a theoretical description of the electric response of the bulk of the capacitor to an external periodic excitation, establishing the fundamental equations to connect the electrical impedance response of the cell with the adsorption-desorption phenomena occurring at the surfaces of the electrodes.

A very successful model describing the response of a medium to an external electric field is the so-called diffusional Poisson-Nernst-Planck continuum model, which is particularly useful when we are interested in the electric response of insulators containing ionic impurities by means of the impedance (or immittance) spectroscopy technique [10, 11, 12]. It describes the distribution of ions due to an external electric field in terms of drift-diffusion equations for both type of ions coupled with the Poisson equation for the electric potential across the sample.

The resulting partial differential equations have to be solved with the proper boundary conditions for the electric potential and the ionic current densities on the electrodes. This model has been investigated for systems confined between completely blocking electrodes [13], and has been applied to a series of relevant problems in the last decades [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. Here, to keep the theoretical framework as general as possible, we solve the fundamental equations for the general case of drift-diffusing cations and anions (ambipolar diffusion) and for two different adsorbing-desorbing electrodes, i.e. an asymmetric cell.

3.1. Bulk response of the cell to external excitation

Let us consider a liquid, of dielectric constant ε, containing one group of positive and one group of negative ions of elementary electric charge, q . In thermodynamic equilibrium, in the absence of external field, the ions are uniformly distributed across the cell with a bulk density of positive, n_p, and negative ones, n_m, such that $n_p = n_m = n_0$. The presence of an external field is responsible for a non-homogeneous distribution of ions, $n_p \neq n_0$ and $n_m \neq n_0$. In this situation, the bulk density of ionic currents are due to drift and diffusion. In the Einstein-Smoluchowski approximation, the current densities are given by

$$\mathbf{j}_p = -D_p \left(\nabla n_p - \frac{q n_p}{K_B T} \mathbf{E} \right), \tag{1}$$

$$\mathbf{j}_m = -D_m \left(\nabla n_m + \frac{q n_m}{K_B T} \mathbf{E} \right), \tag{2}$$

where D_p and D_m are the diffusion coefficients of the positive and negative ions in the considered insulating liquid, respectively, $K_B T$ is the thermal energy, and $\mathbf{E}$ is the electric field. The equations of continuity, stating the conservation of the number of ions, in the absence of generation and recombination, are

$$\frac{\partial n_p}{\partial t} = -\nabla \cdot \mathbf{j}_p, \tag{3}$$

$$\frac{\partial n_m}{\partial t} = -\nabla \cdot \mathbf{j}_m. \tag{4}$$

The Poisson equation, relating the actual electric field in the sample with the ionic charge is

$$\nabla \cdot \mathbf{E} = \frac{q}{\varepsilon}(n_p - n_m). \tag{5}$$

To carry on the calculations, we consider a sample in the shape of a slab, of thickness d, limited by two flat electrodes, just in order to treat the problem as one-dimensional. All the structures of the electrodes resulting from their porosity are taken into account in the effective adsorption parameters of the kinetic equations used as boundary conditions for the bulk equations. It follows that in this framework all physical quantities entering the description of the system are actually averaged values of the real ones performed in the plane perpendicular the equivalent electrodes. Furthermore, the frequency of the external field is assumed so low that $\mathbf{E} = -\nabla V$. The Cartesian reference frame used for the mathematical description has the $z-$axis normal to the electrodes, one of them placed at $z = -d/2$ (electrode A) and another one at $z = d/2$ (electrode B). The external applied difference of potential is kept small enough to assure that, in the bulk, $(n_p - n_0)/n_0 \ll 1$ as well as $(n_m - n_0)/n_0 \ll 1$. In this framework of a linear bulk behaviour, the continuity Eqs. (3) and (4) can be rewritten as

$$\begin{aligned} \frac{\partial n_p}{\partial t} &= D_p\left(\frac{\partial^2 n_p}{\partial z^2} + \frac{n_0 q}{K_B T}\frac{\partial^2 V}{\partial z^2}\right), \qquad (6) \\ \frac{\partial n_m}{\partial t} &= D_m\left(\frac{\partial^2 n_m}{\partial z^2} - \frac{n_0 q}{K_B T}\frac{\partial^2 V}{\partial z^2}\right), \qquad (7) \end{aligned}$$

and the Poisson equation as

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}\left(n_p - n_m\right). \tag{8}$$

For further consideration it is useful to introduce the reduced quantities

$$u_p = \frac{n_p - n_0}{n_0}, \quad u_m = \frac{n_m - n_0}{n_0}, \quad \text{and} \quad u_v = \frac{V}{v_t}. \tag{9}$$

where $v_t = K_B T/q$ is the thermal voltage, of the order of 0.025V, for univalent ions. In terms of these quantities, Eqs. (6) and (7) become, respectively,

$$\frac{\partial u_p}{\partial t} = D_p \left(\frac{\partial^2 u_p}{\partial z^2} + \frac{\partial^2 u_v}{\partial z^2} \right), \qquad (10)$$

$$\frac{\partial u_m}{\partial t} = D_m \left(\frac{\partial^2 u_m}{\partial z^2} - \frac{\partial^2 u_v}{\partial z^2} \right), \qquad (11)$$

and

$$\frac{\partial^2 u_v}{\partial z^2} = -\frac{1}{\Lambda^2} (u_p - u_m), \qquad (12)$$

where $\Lambda = \sqrt{\varepsilon v_t/(n_0 q)}$ is proportional to the Debye length. In the Appendix, we present the solutions of this set of fundamental equations in the presence of a harmonic external voltage. It is then possible to obtain analytically the electrical impedance $Z(\omega)$, given by Eq. (61), for the case of a sample characterised by asymmetric surfaces.

3.2. Adsorption in the presence of bias

According to the Langmuir adsorption isotherm, the kinetic equation describing adsorption process is

$$\frac{d\sigma}{dt} = kn - \frac{1}{\tau}\sigma, \qquad (13)$$

where n is the bulk density of adsorbable particles just in front of the adsorbing surface and σ is the surface density of adsorbed particles. The parameters k and τ are known as adsorbing coefficient and desorption time, respectively. We are interested in the case in which the adsorbed particles are ions dissolved in an insulating liquid. In this case a kinetic equation of type (13) is valid for the positive, p, and negative, m, ions. We assume that in the absence of an external bias the medium is locally and globally neutral, and that the bulk densities of ions is n_0, with an electric charge q. In the presence of an external bias, the local equilibrium close to the electrode is perturbed because the bulk densities of positive and negative ions just in front of the electrode are changed. In this case Eq. (13) for the positive ions, just in front of the electrode at $z = d/2$, at the potential $V(d/2, t)$ imposed by the external bias, is

$$\frac{d\delta\sigma_p}{dt} = k_p \delta n_p - \frac{1}{\tau_p}\delta\sigma_p, \tag{14}$$

indicating by $\delta\sigma_p$ and δn_p the variations of the surface density of adsorbed and bulk density of positive ions due to the presence of the bias. The variation of the bulk density of positive ions, just in front of the adsorbing electrodes, is given by

$$\delta n_p(d/2,t) = n_p(d/2,t) - n_0 = n_0 \left\{ e^{-u(d/2,t)} - 1 \right\}, \tag{15}$$

where $u(d/2,t)$ is related to the external bias by

$$u(d/2,t) = b\frac{V(d/2,t)}{2v_t}. \tag{16}$$

The value of b is connected with the average thickness, L, of the material deposited on the electrode, whose dielectric constant is ε_s. Thus, a rough estimation of its value, when $L \ll d$, is

$$b \approx 2\frac{\varepsilon}{\varepsilon_s}\frac{L}{d}, \tag{17}$$

and it is expected to be smaller than 1. For the negative ions an analysis of the same kind gives

$$\delta n_m(d/2,t) = n_m(d/2,t) - n_0 = n_0 \left\{ e^{u(d/2,t)} - 1 \right\}. \tag{18}$$

Similar considerations hold for the electrode at $z = -d/2$, at the electric potential $V(-d/2,t)$.

In the following we consider the case relevant from the experimental point of view in which the bias

$$V(t) = V(d/2,t) - V(-d/2,t) \tag{19}$$

is a periodic function of t with period T and amplitude V_0, of the type

$$V(t) = \begin{cases} 2(V_0/T)t & \text{for } 0 \le t \le T/2 \\ 2V_0 - 2(V_0/T)t & \text{for } T/2 \le t \le T, \end{cases} \tag{20}$$

whose average value on one period is not zero, i.e., the cell is polarised. It can be expanded in Fourier series as

$$V(t) = \frac{V_0}{2} + \sum_{n=-\infty}^{\infty} V_n e^{in\omega_0 t}, \tag{21}$$

with the Fourier coefficients

$$V_n = -\frac{1-(-1)^n}{(n\pi)^2}\, V_0, \tag{22}$$

where $\omega_0 = 2\pi/T$. Since $V(t) = V(t+T)$, as well as $u(t) = u(t+T)$, the function

$$\psi_p[u(t)] = e^{-u(t)} - 1 \tag{23}$$

entering in δn_p is also periodic with the same period T, and it can be decomposed in Fourier series as follows:

$$\psi_p(t) = \sum_{n=-\infty}^{\infty} H_{pn}\, e^{in\omega_0 t}, \tag{24}$$

where

$$H_{pn} = \frac{1}{T}\int_0^T \left(e^{-u(t)} - 1\right) e^{-in\omega_0 t}\, dt. \tag{25}$$

A simple calculation gives

$$H_{pn} = b\frac{1-(-1)^n\, e^{-bu_0}}{(n\pi)^2 + (bu_0)^2}\; u_0. \tag{26}$$

Considerations similar to those done for the positive ions are valid also for the negative ions. In this case

$$\delta n_m = n_m - n_0 = n_0\left(e^u - 1\right) = n_0 \psi_m(u). \tag{27}$$

Operating as for the positive ions we get for the Fourier coefficients of $\psi_m(t)$ the expression

$$H_{mn} = -b\frac{1-(-1)^n\, e^{bu_0}}{(n\pi)^2 + (bu_0)^2}\; u_0. \tag{28}$$

Decomposing $\delta\sigma_p$ in Fourier series

$$\delta\sigma_p = \sum_{n=-\infty}^{\infty} \delta\sigma_{pn}\, e^{in\omega_0 t}, \tag{29}$$

and using Eq. (14) we get for $\delta\sigma_{pn}$ for a non-alternating excitation

$$\delta\sigma_{pn} = n_0 k_p \tau_p \frac{H_{pn}}{1 + in\omega_0\tau_p}. \tag{30}$$

In dynamical regime, the sources of adsorbable particles are the current densities of particles coming from the bulk, giving rise to the balance equations

$$j_p = \frac{d\delta\sigma_p}{dt} \quad \text{and} \quad j_m = \frac{d\delta\sigma_m}{dt}, \tag{31}$$

at the limiting surfaces. In the Fourier space, taking into account (30), Eq. (31) can be rewritten, for the non-alternating case under consideration, as

$$j_{pn} = n_0 k_p \, \frac{in\omega_0\tau_p}{1 + in\omega_0\tau_p} \, H_{pn}. \tag{32}$$

Repeating step by step the same calculations for the negative ions we get

$$j_{mn} = n_0 k_m \, \frac{in\omega_0\tau_m}{1 + in\omega_0\tau_m} \, H_{mn}. \tag{33}$$

Equations (32) and (33) play the role of boundary conditions in the Poisson-Nernst-Planck model. In this case, the boundary conditions by means of which the integration constants C_{p1}, C_{p2}, C_{p3}, C_{p4}, C_v and C_{v1} can be evaluated are

$$\begin{aligned} \phi'_{pn} + \phi'_{vn} &= R_{pn}, & (34)\\ \phi'_{mn} - \phi'_{vn} &= R_{mn}, & (35)\\ \phi_{vn} &= \pm(1-b)V_n & (36) \end{aligned}$$

for $z = \pm d/2$, where

$$R_{pn} = -\frac{k_p}{D_p} \, \frac{in\omega_0\tau_p}{1 + in\omega_0\tau_p} \, H_{pn}, \tag{37}$$

$$R_{mn} = -\frac{k_m}{D_m} \, \frac{in\omega_0\tau_m}{1 + in\omega_0\tau_m} \, H_{mn}. \tag{38}$$

The adsorption parameters k_p, τ_p, k_m, and τ_m can be different for the two surfaces. From now on the calculations are standard and are reported in the Appendix.

4. Fitting of the experimental data

To test our model, based on the generalisation of the Langmuir model, we compare our theoretical predictions with the experimental data obtained on cells limited by electrodes treated as discussed in Sec. 2, submitted to a non-alternating external excitation. To fit the experimental data, we decompose the excitation (20) in Fourier series, as in (21), where V_n are given by (22). In the linear approximation the current is given by

$$I = \sum_{n=-\infty}^{\infty} I_n e^{in\omega_0 t}, \tag{39}$$

where $I_n = V_n/Z_n$, with $Z_n = Z(\omega_n)$, given by (61), and $\omega_n = n\omega_0$. The physical parameters entering the Poisson-Nernst-Planck model are $D_p = 1.61 \times 10^{-9}\,\mathrm{m^2/s}$, $D_m = 1.05 \times 10^{-9}\,\mathrm{m^2/s}$, $\varepsilon = 80\varepsilon_0$, where ε_0 is the permittivity of the empty space [30], $n_0 = 6.06 \times 10^{26}\ \mathrm{m^{-3}}$, and the geometrical parameters of the cell are $d = 5.5 \times 10^{-3}\,\mathrm{m}$ and $S = 1.21 \times 10^{-4}\,\mathrm{m^2}$. The fits have been done for different values of the period of the external excitation, T, namely 20 s, 40 s, 53 s, and 80 s, and for the amplitude of the bias potential from 0.2 V to 1.2 V, with 0.2 V steps. The parameter b related to the screening effect on the potential has, for all fitted data, the same value, 0.02. Assuming $\varepsilon_s \approx 10\varepsilon_0$ [31], and $L \approx 5 \times 10^{-6}\,\mathrm{m}$ (see Fig. 2), from Eq. (17) we get $b \approx 0.016$ whose order of magnitude well compare with the best fit value. For each pair of T and V_0 we chose the values of k's and τ's that gave the best approximation to the data. The complete set of fitting parameters are presented in the Table reported in the Appendix.

In Fig. 3, the electric current of the cell is shown for different amplitudes of the bias potential. For illustrative purposes, only the experimental results for the period $T = 53\,\mathrm{s}$ are exhibited. The agreement between the predictions of the model with the experimental data is very good for all the amplitudes of the bias potential applied to the cell during the measurements.

In Fig. 4, the $I(V)$ curves obtained for the same bias amplitudes as the ones in Fig. 3, when $T = 53\,\mathrm{s}$, are report. The agreement between the theo-

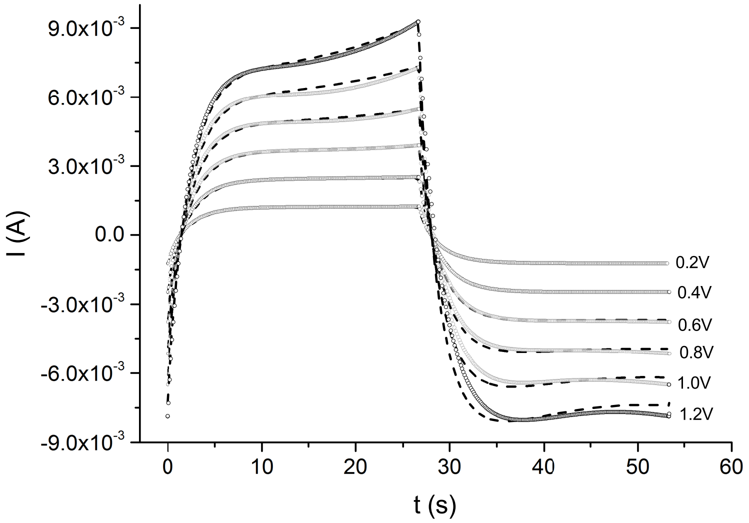

Figure 3: Time dependence of the electric current of the cell under different amplitudes of the applied bias potential. The period of the external excitation is $T = 53\,\mathrm{s}$. Dashed curves are the best fit of the experimental data (empty circles) obtained with Eq. (39), where Z_n is reported in Eq. (61).

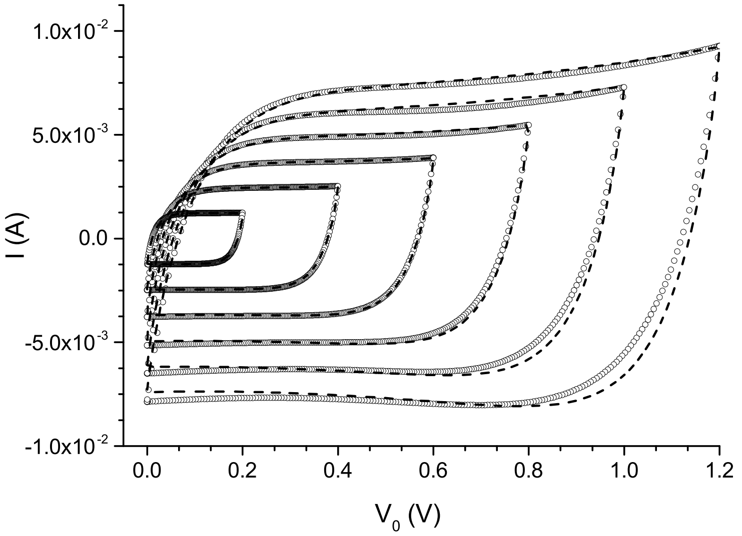

Figure 4: Parametric curve $I = I(V)$ for the cell submitted to a periodic external excitation with $T = 53\,\text{s}$, for different values of the applied potential. Dashed curves are the best fit of the experimental data (empty circles) obtained with Eq. (39), where $Z_n$is reported in Eq. (61).

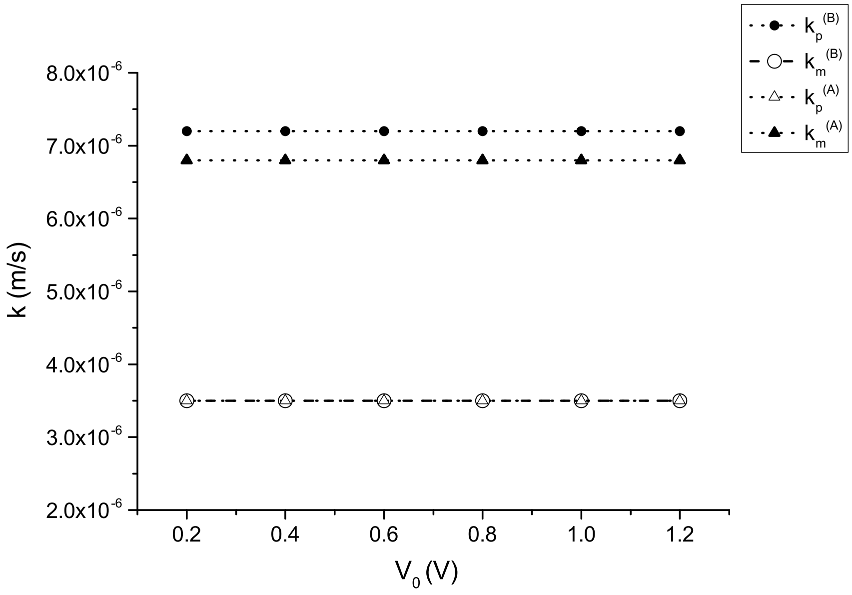

Figure 5: Adsorption coefficients obtained from the best fit procedure, for $T = 53\,\mathrm{s}$. $k_p^{(A)}$, $k_m^{(A)}$, $k_p^{(B)}$ and $k_m^{(B)}$ are the adsorption coefficients on the electrode (A), electrode (B), for the positive, (p), and negative, (m), charges, respectively.

retical model and the experimental results is again very good for the smallest amplitudes, and continues to be rather good even in the case of the largest one ($V_0 = 1.2\,V$). It is worth mentioning that the good agreement has been obtained in correspondence to a very stable set of values of the other fitting parameters, as shown in Figs. 5 and 6. Indeed, the values of the parameters obtained from the best fits show a remarkable stability for each pair T and V_0. They are practically the same as could be seen in these figures and also inspecting the Table in the Appendix.

In Fig. 5, $k_p^{(B)}$ and $k_m^{(A)}$ are, respectively, the adsorption coefficients for positive ions at the electrode (B) and for negative ions at the electrode (A). Their values are practically constant for all amplitudes and are very close in magnitude ($k \approx 7 \times 10^{-6}\,\mathrm{m/s}$), and are of the same order of magnitude as the one reported in Ref. [4]. A corresponding behaviour is found for $k_p^{(A)}$ and $k_m^{(B)}$, but in this case the values are essentially the same ($k \approx 3.5 \times 10^{-6}\,\mathrm{m/s}$) even

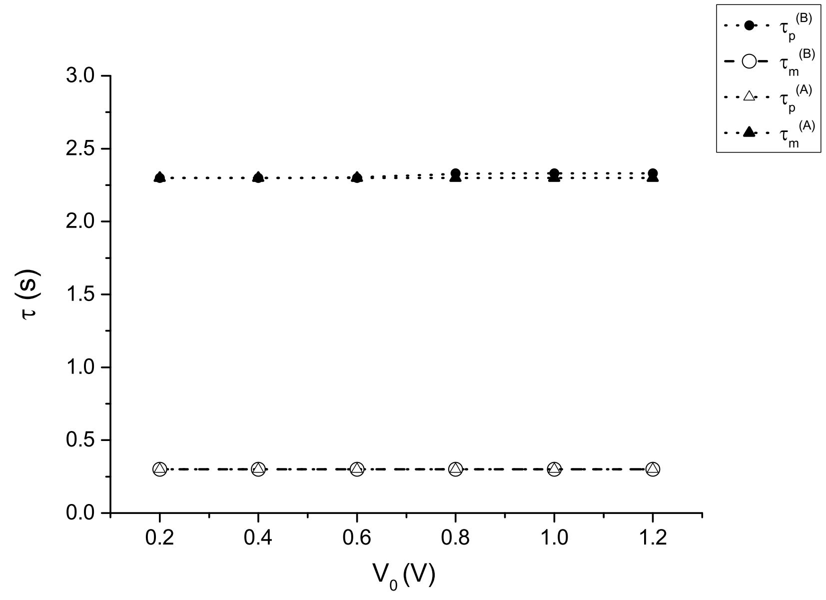

Figure 6: Desorption times obtained from the best fit procedure, for $T = 53\,\mathrm{s}$. $\tau_p^{(A)}$, $\tau_m^{(A)}$, $\tau_p^{(B)}$ and $\tau_m^{(B)}$ are the desorption times on the electrode (A), electrode (B), for the positive, p, and negative, m, charges, respectively.

if smaller than the ones of the previous pair. From the experimental data, it is possible to conclude that the electrode (A) presents a higher effective selectivity for adsorbing the negative charges, while the electrode (B) presents a higher selectivity for adsorbing the positive ones. These results are consistent because in the model the adsorbing rates depend on the screened bias potential on each electrode. They depend also on the physical characteristics of each one of the electrodes, which are adsorbing interfaces even in the absence of any applied potential.

This general conclusion is reinforced by the behaviour of the desorbing times shown in Fig. 6 for the same values of V_0 of Fig. 5. We notice that the desorption process is very rapid for the positive charges adsorbed by the electrode (A) and for the negative charges adsorbed by (B) ($\tau \approx 0.3\,\mathrm{s}$) i.e., in correspondence to a higher adsorption selectivity of these electrodes respectively for negative and positive charges. The desorption process is instead slower for negative charges at the electrode (A) and for the positive ones from electrode (B) ($\tau \approx 2.3\,\mathrm{s}$), i.e., consistently with a correspondingly weaker adsorption rate for these charges. This significant difference in the order of magnitude of the desorption times is due to the fact that the periodic bias potential has a non-vanishing average value. This means that even if the bias is periodic, the electric field always points in the same direction, thus favouring a more rapid desorption at those interfaces where the adsorption process is less intense.

5. Conclusions

We have proposed a model for the ionic adsorption in a capacitive deionisation cell, in the presence of an external electric field. Our approach extends the diffusional Poisson-Nernst-Planck model to non-symmetric cells. It considers a linear bulk behaviour in order to define an electrical impedance in the frequency domain since in the presence of the external field a rapid redistribution of the charges through the cell happens, and a small ac signal approximation is expected to work well. This linear bulk system is in contact with a nonlinear system formed by the interface, i.e., the electrodes. At the interface liquid-electrodes, the adsorption-desorption process takes place and is governed by a generalisation of the Langmuir adsorption model. In this framework, the surface is characterised by a nonlinear behaviour in which the adsorption-desorption rates depends on the screened potential applied to the cell. To test our model we have compared our theoretical predictions with the experimental data relevant to capacitive deionisation cells submitted to a periodic external excitation whose average value is non-vanishing. The best fitting procedure yields a very stable set of adsorption coefficients and desorption times for different amplitudes and periods of the applied potential. The remarkable agreement between the model and the experimental data clearly indicates that the theoretical considerations are quite consistent with the physicochemical phenomena within the cells.

Appendix

Solutions of the Poisson-Nernst-Planck equations

To search for the solutions of the linear Eqs. (10), (11), and (12), in the presence of an harmonic excitation, we may assume they have the form [11]:

$$(u_p, u_m, u_v)(z,t) = (\phi_p, \phi_m, \phi_v)(z)\ \exp(i\omega t). \tag{40}$$

In this framework Eqs. (10), (23), and (24) can be rewritten as

$$\begin{aligned} i\omega\phi_p &= D_p(\phi'' + \phi_v''), && (41)\\ i\omega\phi_m &= D_m(\phi'' m\phi_v''), && (42) \end{aligned}$$

and

$$\phi_v'' = -\frac{1}{\Lambda^2}\,(\phi_p - \phi_m), \tag{43}$$

where $f' = df/dz$. Substituting Eq. (43) into (41) and (42), we get

$$\begin{aligned} \phi_p'' - \beta_p^2\,\phi_p + \frac{1}{\Lambda^2}\,\phi_m &= 0, && (44)\\ \phi_m'' - \beta_m^2\,\phi_m + \frac{1}{\Lambda^2}\,\phi_p &= 0, && (45) \end{aligned}$$

where

$$\begin{aligned} \beta_p^2 &= \frac{1}{\Lambda^2}\left(1 + i\omega\,\frac{\Lambda^2}{D_p}\right), && (46)\\ \beta_m^2 &= \frac{1}{\Lambda^2}\left(1 + i\omega\,\frac{\Lambda^2}{D_m}\right). && (47) \end{aligned}$$

Solutions of the ordinary differential equations (44) and (45) are of the type

$$\begin{aligned} \phi_p &= C_{pa}\,\sinh(\mu z) + C_{pb}\,\cosh(\mu z), && (48)\\ \phi_m &= C_{ma}\,\sinh(\mu z) + C_{mb}\,\cosh(\mu z), && (49) \end{aligned}$$

where C_{pa}, C_{pb}, C_{ma} and C_{mb} are integration constants to be determined by the boundary conditions, and the wave-vectors μ are given by the bi-quadratic equation

$$\mu^4 - (\beta_p^2 + \beta_m^2)\mu^2 + \beta_p^2\,\beta_m^2 - \frac{1}{\Lambda^4} = 0. \tag{50}$$

A simple calculation gives

$$\mu_{1,2} = \frac{1}{L}\sqrt{\frac{(\beta_p^2+\beta_m^2)L^2 \pm \sqrt{4+(\beta_p^2+\beta_m^2)\Lambda^4}}{2}}. \tag{51}$$

It follows that

$$\begin{aligned}
\phi_p &= C_{p1}\sinh(\mu_1 z) + C_{p2}\sinh(\mu_2 z) + \\
&+ C_{p3}\cosh(\mu_1 z) + C_{p4}\cosh(\mu_2 z), & (52)\\
\phi_m &= -k_1 C_{p1}\sinh(\mu_1 z) - k_2 C_{p2}\sinh(\mu_2 z) + \\
&- k_1 C_{p3}\cosh(\mu_1 z) - k_2 C_{p4}\cosh(\mu_2 z), & (53)
\end{aligned}$$

and

$$\begin{aligned}
\phi_v &= -\frac{1+k_1}{\Lambda^2\mu_1^2}[C_{p1}\sinh(\mu_1 z) + C_{p3}\cosh(\mu_1 z)] \\
&- \frac{1+k_2}{\Lambda^2\mu_2^2}[C_{p2}\sinh(\mu_2 z) + C_{p4}\cosh(\mu_2 z)] \\
&+ C_v z + C_{v1} & (54)
\end{aligned}$$

where

$$k_1 = \Lambda^2(\mu_1^2 - \beta_p^2), \quad \text{and} \quad k_2 = \Lambda^2(\mu_2^2 - \beta_p^2). \tag{55}$$

The integration constants C_{p1}, C_{p2}, C_{p3}, C_{p4}, C_v and C_{v1} are determined by means of the boundary conditions of the problem imposed on the current densities of positive and negative ions and on the electric potential at $z = \pm d/2$. In our framework current densities of positive and negative ions are given by

$$\begin{aligned}
j_p &= -n_0 D_p(\phi_p' + \phi_v')\,\exp(i\omega t), & (56)\\
j_m &= -n_0 D_m(\phi_m' - \phi_v')\,\exp(i\omega t), & (57)
\end{aligned}$$

whereas the displacement current $j_D = \varepsilon \partial E/\partial t$ is

$$j_D = -i\omega v_t \phi_v' \,\exp(i\omega t). \tag{58}$$

The total electric current density across the sample is then

$$j = q(j_p - j_m) + j_D, \tag{59}$$

that using the result reported above can be written as

$$j = -n_0 q C_v (D_p + D_m + i\Lambda^2\omega)\ \exp(i\omega t). \tag{60}$$

It depends just on the integration constant C_v, related to the linear dependence of ϕ_v on z-coordinate.

In the linear case under investigation, when the external electric excitation is a period function of time of the type $V(t) = V_0 \exp(i\omega t)$, the impedance of the cell is defined as $Z = V(t)/jS$ such that

$$Z(\omega) = -\frac{u_0}{n_0 q C_v (D_p + D_m + i\Lambda^2\omega)S} \tag{61}$$

where S is the surface area of the electrodes and $u_0 = V_0/v_t$. The constant C_V together with the other integration constants are determined using the boundary conditions Eqs. (34), (35), and (36).

Fitting parameters

The best fitting parameters are shown in the Table below for different values of the period T. They validate the model proposed by us, demonstrating its robustness in the whole range of experimental measurements.

T	V_0	$k_p^{(B)}$	$k_p^{(A)}$	$k_m^{(B)}$	$k_m^{(A)}$	$\tau_p^{(B)}$	$\tau_p^{(A)}$	$\tau_m^{(B)}$	$\tau_m^{(A)}$
s	V	$10^{-6}\ m/s$	$10^{-6}\ m/s$	$10^{-6}\ m/s$	$10^{-6}\ m/s$	s	s	s	s
20	0.2	7.1	3.0	3.0	7.2	2.1	0.35	0.35	2.1
20	0.4	7.1	3.0	3.0	7.1	2.1	0.34	0.34	2.1
20	0.6	7.0	3.0	3.0	7.1	1.95	0.3	0.3	2.15
20	0.8	7.3	3.0	3.0	6.8	2.1	0.3	0.3	2.5
20	1.0	7.2	3.5	3.5	6.8	2.2	0.3	0.3	2.2
20	1.2	7.1	3.5	3.5	6.8	2.2	0.3	0.3	2.2
40	0.2	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
40	0.4	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
40	0.6	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
40	0.8	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
40	1.0	7.3	3.5	3.5	6.8	2.25	0.3	0.3	2.3
40	1.2	7.3	3.5	3.5	6.75	2.25	0.3	0.3	2.3
53	0.2	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
53	0.4	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
53	0.6	7.2	3.5	3.5	6.8	2.3	0.3	0.3	2.3
53	0.8	7.2	3.5	3.5	6.8	2.33	0.3	0.3	2.3
53	1.0	7.2	3.5	3.5	6.8	2.33	0.3	0.3	2.3
53	1.2	7.2	3.5	3.5	6.8	2.33	0.3	0.3	2.3
80	0.2	7.25	3.5	3.5	6.9	2.35	0.3	0.3	2.2
80	0.4	7.25	3.5	3.5	6.9	2.35	0.3	0.3	2.2
80	0.6	7.25	3.5	3.5	6.9	2.33	0.3	0.3	2.3
80	0.8	7.25	3.5	3.5	6.9	2.33	0.3	0.3	2.3
80	1.0	7.25	3.5	3.5	6.9	2.33	0.3	0.3	2.3
80	1.2	7.2	3.5	3.5	6.9	2.33	0.3	0.3	2.3

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