I. DETAILED DERIVATION OF EQ. 1 OF THE MANUSCRIPT

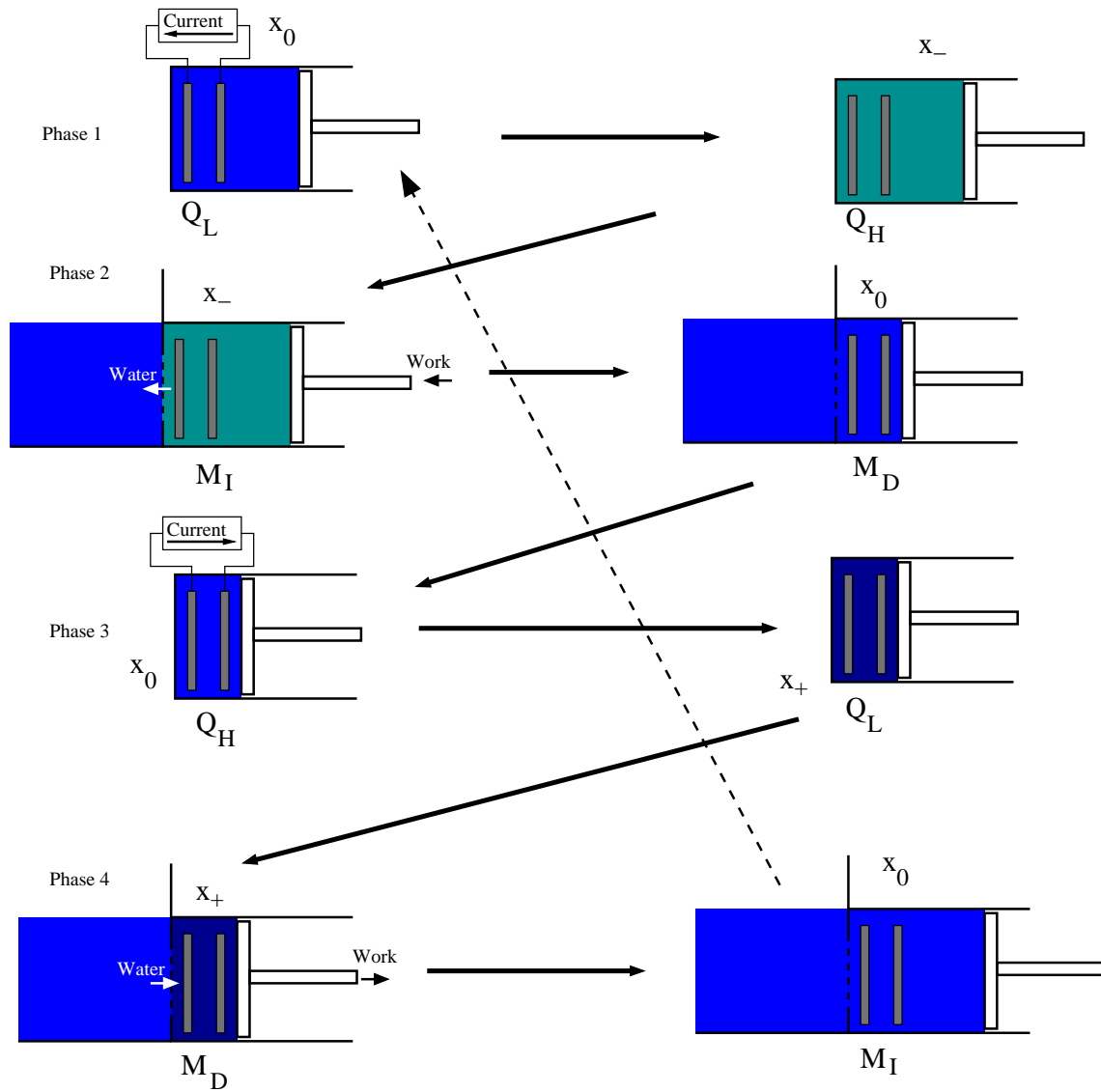## A. Description of the four-step reversible cycle

For our purposes, the behaviour of the generic cell is described by the potential $V(Q, x)$ between the electrodes, and by the mass of adsorbed salt $W(Q, x)$, both considered as functions of the total accumulated charge Q and of the bulk mass fraction of ions x. In the following, the masses of adsorbed salt, solute and solvent are expressed in moles, and thus the mass fraction is expressed as the ratio between the moles of solute and the moles of the solvent ($x = N/M$).

The cycle starts with a mass fraction $x = x_0$ of the solution in the cell, and with initial values of solvent mass in the cell $M = M_I$ and accumulated charge $Q = Q_L$. The phases of the cycle are the following:

1. The electrodes are charged, by making a current flow through the cell, so that the charge Q increases from Q_L to Q_H. Salt is adsorbed from the solution into the electrodes, partially de-ionizing it. The final concentration becomes $x_- < x_0$.

2. The circuit is opened, and the cell is put into contact with the reservoir through the semipermeable membrane. The osmotic flow decreases the mass of the solvent in the cell, M, from M_I to M_D, because the concentration in the cell, x_-, is lower than x_0. A mechanical work is done by osmosis. At the end of the process, the concentration x in the cell becomes equal to the concentration in the reservoir x_0.

3. The electrodes are discharged, by making a current flow, so that the charge Q decreases from Q_H to Q_L. The desorption of ions from the electrodes increases the concentration of the solution in the cell. The final concentration becomes $x_+ > x_0$.

4. The circuit is opened, and the cell is put again into contact with the reservoir, through the semipermeable membrane. The mass of the solvent in the cell, M, increases from M_D to M_I due to the osmotic flow. The concentration becomes equal to x_0.

The reversible cycle is schematically presented below.

Phase	Concentration x	Charge Q	Mass M
1	$x_0 \to x_-$	$Q_L \to Q_H$	M_I
2	$x_- \to x_0$	Q_H	$M_I \to M_D$
3	$x_0 \to x_+$	$Q_H \to Q_L$	M_D
4	$x_+ \to x_0$	Q_L	$M_D \to M_I$

Phase 1 — x_0 Current — Q_L → x_- Q_H

Phase 2 — x_- Water — Work M_I → x_0 Work M_D

Phase 3 — Current x_0 Q_H → x_+ Q_L

Phase 4 — x_+ Water — Work M_D → x_0 M_I

The following graph shows the cycle in the charge-mass-concentration (red line). The other lines represent the projections on the charge-mass, charge-concentration and mass-concentration planes.
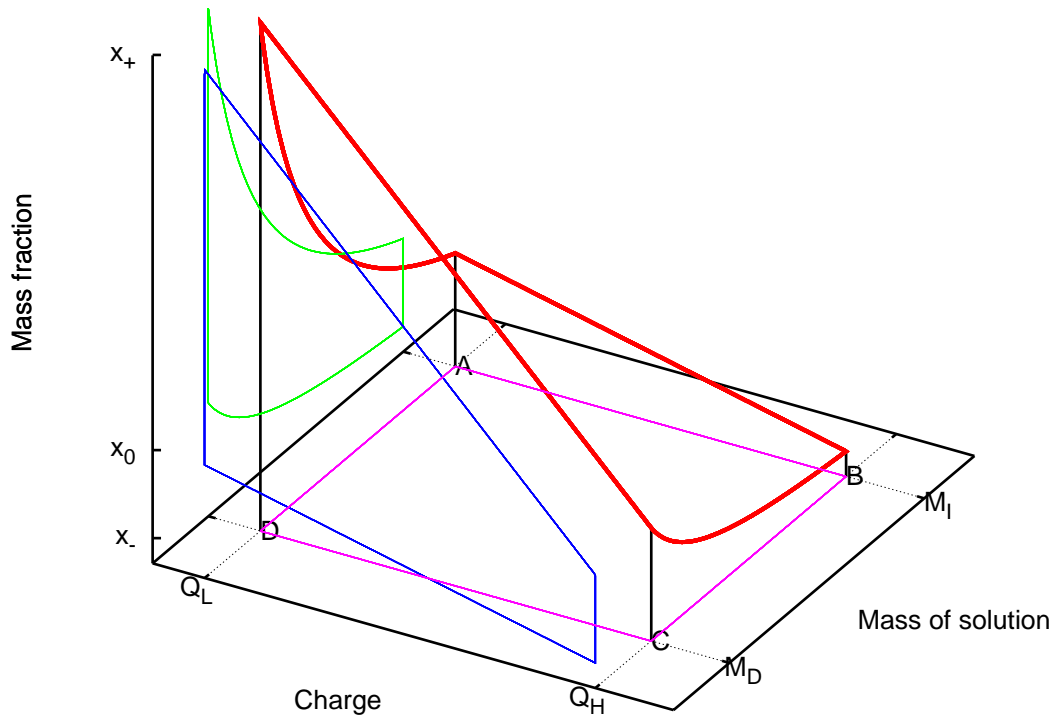
The plotted cycle is only representative, and does not correspond to a real experimental situation. The phases 1, 2, 3 and 4 are represented respectively by the curves A-B, B-C, C-D, D-A.

Projections of the cycle on the concentration-charge plane and concentration-mass plane are shown in the following graphs.
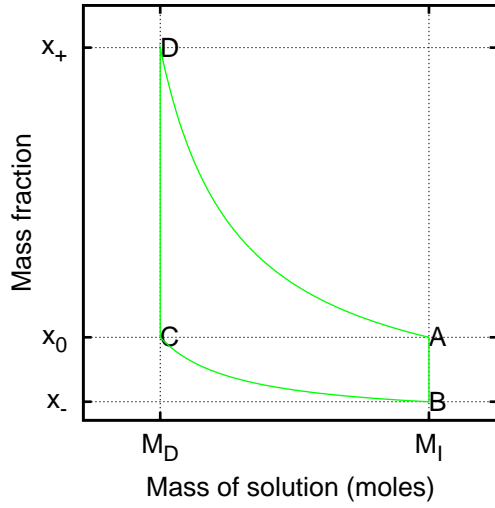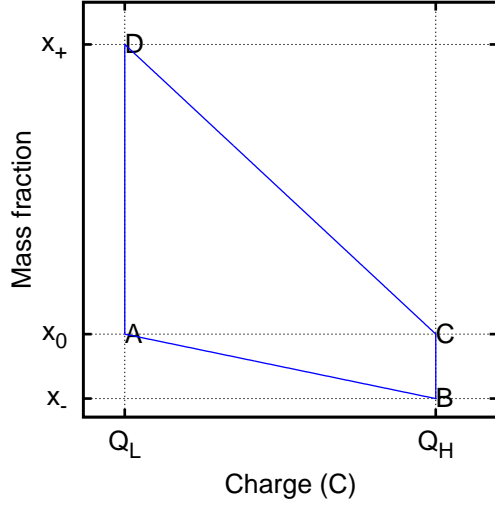
B.   Derivation of the relation

None of the phases involves a change of the mass of the solute inside the cell, and thus we can write the following equations, which express the conservation of the solute mass in the cell at the end of the four phases:

$$x_- M_I + W(Q_H, x_-) = S$$
$$x_0 M_D + W(Q_H, x_0) = S$$
$$x_+ M_D + W(Q_L, x_+) = S$$
$$x_0 M_I + W(Q_L, x_0) = S, \qquad (1)$$

where S is the mass in moles of the solute in the cell.

We assume that x_0, Q_L, Q_H and M_I are the independent parameters of the system, that can be chosen independently. The quantities x_+, x_-, M_D and S are the dependent parameters of the system, and can be calculated by means of Eqs. 1.

In the following, we will implicitly assume that all the dependent parameters are functions of Q_H, and we will call p' the derivative of the dependent parameter p with respect to Q_H. Anyhow, from the last of Eqs. 1, it can be seen immediately that S actually does not depend on Q_H, and thus $S' = 0$.

The salt concentration in the cell depends on the quantity that is changed during each phase, i.e., Q in phases 1 and 3, and M in phases 2 and 4. The equations expressing the conservation of the solute mass in the cell during the

four phases are the following:

$$x_1(Q) M_I + W[Q, x_1(Q)] = S$$
$$x_2(M) M + W[Q_H, x_2(M)] = S$$
$$x_3(Q) M_D + W[Q, x_3(Q)] = S$$
$$x_4(M) M + W[Q_L, x_4(M)] = S. \tag{2}$$

These equations implicitly define the variation of mass fraction during each phase.

The energies consumed in the four phases are the following:

$$\Delta E_1 = \int_{Q_L}^{Q_H} V[Q, x_1(Q)] \, \mathrm{d}Q$$

$$\Delta E_2 = \int_{M_I}^{M_D} \{\Pi[x_2(M)] - \Pi(x_0)\} \, \mathrm{d}M$$

$$\Delta E_3 = \int_{Q_H}^{Q_L} V[Q, x_3(Q)] \, \mathrm{d}Q$$

$$\Delta E_4 = \int_{M_D}^{M_I} \{\Pi[x_4(M)] - \Pi(x_0)\} \, \mathrm{d}M, \tag{3}$$

where $\Pi(x)$ is the osmotic pressure of ions in the bulk solution, with mass fraction x.

As the cycle is thermodynamically reversible and isothermal, i.e. it exchanges heat towards a single heat reservoir, the relation connecting $V(Q, x)$ and $W(Q, x)$ is obtained by equating to zero the sum of the energies consumed in each phase:

$$\Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 = 0, \tag{4}$$

We consider the limit $Q_H \to Q_L$, where $x_0 = x_+ = x_- = x_1(Q) = x_2(M) = x_3(Q) = x_4(M)$ and $M_D = M_I$. In that limit, both Eq. 4 and its derivative with respect to Q_H become identically 0.

The first derivatives of Eq. 3 with respect to Q_H must be calculated. The results are:

$$\Delta E_1' = V[Q_H, x_-] + \int_{Q_L}^{Q_H} \partial_x V[Q, x_1(Q)] \, x_1'(Q) \, \mathrm{d}Q \tag{5}$$

$$\Delta E_2' = \int_{M_I}^{M_D} \partial_x \Pi[x_2(M)] \, x_2'(M) \, \mathrm{d}M \tag{6}$$

$$\Delta E_3' = -V[Q_H, x_0] + \int_{Q_H}^{Q_L} \partial_x V[Q, x_3(Q)] \, x_3'(Q) \, \mathrm{d}Q \tag{7}$$

$$\Delta E_4' = -[\Pi(x_+) - \Pi(x_0)] M_D' + \tag{8}$$

$$\int_{M_D}^{M_I} \partial_x \Pi[x_4(M)] \, x_4'(M) \, \mathrm{d}M \tag{9}$$

The first derivatives of Eq. 3 with respect to Q_H, in the limit $Q_H \to Q_L$, are:

$$\lim \Delta E_1' = V[Q_L, x_0] \tag{10}$$
$$\lim \Delta E_2' = 0 \tag{11}$$
$$\lim \Delta E_3' = -V[Q_L, x_0] \tag{12}$$
$$\lim \Delta E_4' = 0. \tag{13}$$

The sum of those four terms is identically 0. The second derivatives of Eq. 3 with respect to Q_H, in the limit $Q_H \to Q_L$, are:

$$\lim \Delta E_1'' = \partial_Q V(Q_L, x_0) + \partial_x V(Q_L, x_0) x_-' + \partial_x V(Q_L, x_0) x_1'(Q_L)$$
$$\lim \Delta E_2'' = \partial_x \Pi(x_0) x_2'(M_I) M_D'$$
$$\lim \Delta E_3'' = -\partial_Q V(Q_L, x_0) - \partial_x V(Q_L, x_0) x_3'(Q_L)$$
$$\lim \Delta E_4'' = -\partial_x \Pi(x_0) [x_+' + x_4'(M_I)] M_D'. \tag{14}$$

Equating the sum of these four terms to zero leads to the following equation:

$$\partial_x V\left(Q_L, x_0\right)\left[x'_- + x'_1\left(Q_L\right) - x'_3\left(Q_L\right)\right] = \partial_x \Pi\left(x_0\right) M'_D\left[x'_+ + x'_4\left(M_I\right) - x'_2\left(M_I\right)\right] \tag{15}$$

Now it is necessary to calculate the derivatives of the concentrations and of M_D with respect to Q_H. The first derivatives of Eqs. 1 are:

$$x'_- M_I + \partial_Q W\left(Q_H, x_-\right) + \partial_x W\left(Q_H, x_-\right) x'_- = 0 \tag{16}$$

$$x_0 M'_D + \partial_Q W\left(Q_H, x_0\right) = 0$$

$$x'_+ M_D + x_+ M'_D + \partial_x W\left(Q_L, x_+\right) x'_+ = 0. \tag{17}$$

The fourth equation is neglected, because it is an identity. Making again the limit $Q_H \to Q_L$ and solving, we obtain $M'_D = -\partial_Q W\left(Q_L, x_0\right)/x_0$, $x'_- = -\chi$ and $x'_+ = \chi$, where $\chi = \partial_Q W\left(Q_L, x_0\right)/\left[M_I + \partial_x W\left(Q_L, x_0\right)\right]$.

Similarly, the first derivatives of Eqs. 2 are:

$$x'_1\left(Q\right) M_I + \partial_x W\left[Q, x_1\left(Q\right)\right] x'_1\left(Q\right) = 0 \tag{18}$$

$$x'_2\left(M\right) M + \partial_Q W\left[Q_H, x_2\left(M\right)\right] + \partial_x W\left[Q_H, x_2\left(M\right)\right] x'_2\left(M\right) = 0 \tag{19}$$

$$x'_3\left(Q\right) M_D + x_3\left(Q\right) M'_D + \partial_x W\left[Q, x_3\left(Q\right)\right] x'_3\left(Q\right) = 0 \tag{20}$$

$$x'_4\left(M\right) M + \partial_x W\left[Q_L, x_4\left(M\right)\right] x'_4\left(M\right) = 0. \tag{21}$$

If we again take the limit $Q_H \to Q_L$ and solve, we obtain $x'_1\left(Q_L\right) = x'_4\left(M_I\right) = 0$, $x'_2\left(M_I\right) = -\chi$ and $x'_3\left(Q_L\right) = \chi$. By substituting these solutions into Eq. 15, we obtain the relation connecting the potential to the salt adsorption:

$$\partial_x V\left(Q, x\right) = \partial_x \Pi\left(x\right) \frac{\partial_Q W\left(Q, x\right)}{x}, \tag{22}$$

The formula is valid for any value of the independent parameters x_0 and Q_L, hence we drop the subscripts L and 0. In the main text, we will refer to specific (per unit mass or surface of electrode) charge and salt adsorption.

II. DETAILS OF THE EXPERIMENTS WITH ACTIVATED CARBON ELECTRODES

The comparison presented in Fig. 2 of the main paper is based on data already reported in literature [1], concerning a CDI experiment with activated carbon electrodes.

The data presented Ref. [1] have been extracted from the graphs presented in Fig. 2 of that paper. The salt adsorption and the charge stored in the electrodes have been measured for sodium chloride solutions at $C_A = 5$ mM and $C_B = 20$ mM, for various potentials. They are summarized in the following table.

Voltage (V)	Charge (C/g) 5mM	Charge (C/g) 20mM	Salt adsorption (mmol/g) 5mM	Salt adsorption (mmol/g) 20mM
0.2	2.0	2.3	0.007	
0.3	3.2		0.012	
0.4	4.4	5.2	0.025	0.016
0.5	6.1	7.1	0.038	0.026
0.5	5.5	6.1	0.038	0.026
0.6	6.9	8.6	0.043	0.052
0.7	8.3	9.3	0.069	0.059
0.8	9.9	11.7	0.087	0.072
0.9	12.3	13.6	0.103	0.089
1	13.9	14.3	0.118	0.100
1.1		17.6		0.128
1.2	17.7	19.7	0.151	0.143

In order to calculate the data in Fig. 2, we used the following procedure:

1. The curves charge *versus* potential, for the two concentrations, are read as potential *versus* charge curves.

2. The curves potential *versus* charge, for the two concentrations, are interpolated with the polynomials $V_{5mM}(Q) = a_1 Q + a_2 Q^2 + a_3 Q^3$ and $V_{20mM}(Q) = b_1 Q + b_2 Q^2 + b_3 Q^3$.

3. The potential rise ΔV of Eq. 3 of the main paper is calculated as $\Delta V = V_{5mM}(Q) - V_{20mM}(Q)$. Here, the interpolation is needed because the experimental data at different concentrations do not have the same charge Q.

4. From the table, the adsorption *versus* charge curve is extracted. The curve for the lower concentration is interpolated with the polynomial $W(Q) = w_1 Q + w_2 Q^2 + w_3 Q^3$.

5. In order to calculate the differential charge efficiency of Eq. 3, the derivative with respect to Q of this last polynomial was taken: $\eta(Q)/F = w_1 + 2w_2 Q + 3w_3 Q^2$. Here, the interpolation with the polynomial is used as a trick to perform differentiation on experimental data.

The zero-order term of the polynomials used for the interpolation is deliberately set to zero, because all the functions must cross the origin. The other coefficients of the polynomials are reported in the following table.

$V_{5mM}(Q)$	a_1=0.10 V/C	a_2=-0.0035 V/C^2	a_3=7.4×10^{-5} V/C^3
$V_{20mM}(Q)$	b_1=0.084 V/C	b_2=-0.0012 V/C^2	b_3=0
$W(Q)$	w_1=2.7×10^{-6} mol/C	w_2=8.4×10^{-7} mol/C^2	w_3=-2.9×10^{-8} mol/C^3

III. OTHER EDL MODELS

A. Thick EDLs

The modified-Donnan model [2], is applicable inside small micropores, where the EDLs are strongly overlapped and a constant electric potential can be assumed to be present. In this situation, we obtain the following expressions for the dimensionless voltage-charge and salt-charge relations inside the micropores:

$$\Delta\phi_{\mathrm{D}} = \sinh^{-1}\left(\frac{-q_{\mathrm{mi}}}{c}\right) \tag{23}$$

$$w_{\mathrm{mi}}^{\mathrm{excess}} = c\left[\cosh\left(\sinh^{-1}\left(\frac{-q_{\mathrm{mi}}}{c}\right)\right) - 1\right] \tag{24}$$

In this case, the charge q_{mi} and salt $w_{\mathrm{mi}}^{\mathrm{excess}}$ adsorptions are defined as quantities per unit volume, and therefore the total charge and salt stored in the electrodes are $Q = 2eq_{\mathrm{mi}}p_{\mathrm{mi}}V_{\mathrm{electrode}}$ and $W = 2w_{\mathrm{mi}}^{\mathrm{excess}}p_{\mathrm{mi}}V_{\mathrm{electrode}}$, respectively. Here, $V_{\mathrm{electrode}}$ and p_{mi} are the total volume of the electrode and its fraction occupied by micropores, respectively. Eqs. 23 and 24 also verify the relation given by Eq. 4 in the main text when $\nu \to 0$.

[1] R. Zhao, P. M. Biesheuvel, H. Miedema, H. Bruning, and A. van der Wal, J. Phys. Chem. Lett. **1**, 205 (2010).
[2] P. M. Biesheuvel, Y. Fu, and M. Z. Bazant, Phys. Rev. E **83**, 061507 (2011).