Ions Transport and Adsorption Mechanisms in Porous Electrodes During Capacitive-Mixing Double Layer Expansion (CDLE)

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ABSTRACT: A model of the electro-diﬀusion of ions in porous electrodes is applied to analyze the dynamics of capacitive-mixing extraction of energy from salinity gradients with carbon porous electrodes. The complex time-evolution of the cell voltage observed in experiments is satisfactorily described. The asymmetry on the duration of the solution-change steps performed in open circuit is found to be due to the nonlinear voltage–concentration relationship of the electric double layers and to a current that redistributes the counterions along the depth of the electrode leading to nonuniform charge and salt adsorption. The validated model is an essential tool for the design and optimization of renewable energy extraction by this technique.

INTRODUCTION

The recently proposed “capacitive mixing” (CAPMIX) methods to extract energy from salinity gradients are attaining great interest, as they are a very promising strategy to extract reservoirs with diﬀerent salt concentration. The complex time-evolution of the cell voltage observed in experiments is satisfactorily described. The asymmetry on the duration of the solution-change steps performed in open circuit is found to be due to the nonlinear voltage–concentration relationship of the electric double layers and to a current that redistributes the counterions along the depth of the electrode leading to nonuniform charge and salt adsorption. The validated model is an essential tool for the design and optimization of renewable energy extraction by this technique.

CDLE by changing the solution where a pair of charged electrodes are immersed by another solution with lower salinity. If the stored charge is kept constant during the solution change, that is, in open circuit configuration, the capacitance of the EDL decreases, leading to an increase in the cell voltage and of the stored electrostatic energy. A common feature of CAPMIX technologies is the fact that the transport of ions inside the porous electrodes plays a key role in their performance. Therefore, the optimization requires not only the development of accurate EDLs models describing their charge–voltage relationship but also the consideration of the transport of ions inside the porous matrix.

In this work, we apply a 1D theory of the electro-diﬀusion of ions in porous electrodes developed by Biesheuvel and Bazant to analyze the rich physical phenomena observed in experiments with a CDLE prototype cell, which includes the transport, adsorption, and desorption of ions in the porous electrodes. Although some improvements of the model (like faradaic reactions, steric eﬀects, and multi-ions eﬀects or 2D modeling) must be included for a quantitative analysis, the used 1D approach demonstrates to be accurate enough to identify the diﬀerent time scales and transport mechanisms during the CDLE cycle, whose understanding is essential to maximize the power output. The 1D approach has been successfully applied in several previous works devoted to the description of “capacitive deionization” (CDI), a technique that, inversely to CDLE, consumes energy for removing ions from salty water by storing them in the EDLs of a pair of porous carbon electrodes. In fact, it has been recently shown that CDI and CDLE are intrinsically connected.
The full CDLE cycle is as follows\(^2\) (see Figure 1). The CAPMIX cell is submerged in an electrolyte solution of concentration \(C_{\text{saline}}\) (500 mM NaCl in this work) and then externally charged until a voltage difference \(V_{\text{cell}} = V_{\text{ext}}\) is established between its two electrodes. With this initial state, the electrochemical cell is operated performing a four-step cycle: (i) Change the solution from fresh (20 mM NaCl in this work) at constant saline. The dimensionless charge density in the diffuse layer is related to \(\Delta \phi_D\) and \(\Delta \phi_{St}\) through

\[
q_{mi} = -\epsilon_{mi} \sinh \Delta \phi_D = -\frac{\Delta \phi_D}{\delta_{mi}} \quad (2)
\]

where \(\delta_{mi} = (2C_{\text{saline}})/V_{\text{ff}}C_{\text{vol}}\) and \(C_{\text{vol}}\) is a volumetric Stern capacitance. During electrode charging, salt adsorption takes place together with charge adsorption because counterions attraction exceeds the expulsion of co-ions from the EDLs when the condition \(V_0 \ll V_T\) is not verified.\(^3\) This is characterized by the concentration of ions of either type inside the micropores, \(w_{mi} = 1/2(c_{+,mi} + c_{-,mi}) = \epsilon_{mi} \cosh \Delta \phi_D\).

Although eqs 1 and 2 suffice to simulate a CAPMIX cycle like the one shown in Figure 1, they do not inform about the dynamics during the cycle. For this aim, the electro-diffusion of ions inside the porous electrodes has to be taken into account. It can be described by 1D charge and mass balances in the direction \(x\) perpendicular to the electrodes and to the flow in the spacer channel. We distinguish between two regions (see Figure 2): the stagnant diffusion layer (SDL) \((-L_{SDL} < x < 0)\), that is, a transition region out of the electrode matrix where the electric potential and the salt concentration change from their values in the bulk to those inside the electrode,\(^4,5\) and the electrode itself \((0 < x < L_e)\), where charge and salt adsorption have to be taken into account. This treatment leads to the Ohm’s law and the diffusion equation for the ions in the SDL, out of the electrode matrix:\(^6\)

\[
i_{\text{SDL}} = -2Dc_{\text{SDL}} \frac{\partial \phi_{\text{SDL}}}{\partial x} \quad (3)
\]
One-dimensional model of electro-di\textsuperscript{0}fusion of ions in porous electrodes applied to CAPMIX. The uniform rates of charge ($i_{SDL}(t)$) and neutral salt ($c_{SDL}(t)$) transport in the stagnant diffusion layer (SDL) due to gradients of salt concentration and electric potential are modified inside the porous matrix due to adsorption of both charge ($j_{\text{charge}}(x,t)$) and salt ($j_{\text{salt}}(x,t)$) into the EDLs that form at the solid–liquid interface, leading to position- (and time-) dependent quantities $i_{\text{bulk}}(x,t)$ and $i_{\text{bulk}}(x,t)$. The local values of electric potential ($\phi(x,t)$) and salt concentration ($c(x,t)$) determine, together with the adsorbed charge in the EDLs, the (unique) electrode potential through appropriate EDL models. At the beginning of the open circuit steps, the solution in the bulk and in part of the SDL is substituted. The part of the SDL that is not changed instantaneously is determined by the length $L_{\text{change}}$, which is either $C_{\text{saline}}$ or $C_{\text{inlet}}$.

$$\frac{\partial c_{SDL}}{\partial t} = D \frac{\partial^2 c_{SDL}}{\partial x^2}$$

where $i_{SDL} = I_{SDL}/C_{\text{saline}}V_T$ is the dimensionless current density in the SDL (note that it is constant along the whole SDL) and $D$ is the bulk diffusion coefficient.

Inside the porous matrix, these equations have to be modified to include the adsorption rates of charge ($j_{\text{charge}} = \frac{\partial i_{\text{bulk}}}{\partial x}$) and salt ($j_{\text{salt}} = \frac{\partial i_{\text{bulk}}}{\partial t}$) into the EDLs$^{16}$

$$\frac{\partial i_{\text{bulk}}}{\partial x} = - \frac{p_{\text{sal}}}{p_{\text{in}}} \frac{\partial i_{\text{bulk}}}{\partial t}$$

$$\frac{\partial c_{\text{bulk}}}{\partial t} = D_{\text{bulk}} \frac{\partial^2 c_{\text{bulk}}}{\partial x^2} - \frac{p_{\text{sal}}}{p_{\text{in}}} \frac{\partial ^2 i_{\text{bulk}}}{\partial t^2}$$

where $i_{\text{bulk}} = -2D_{\text{bulk}}c_{\text{bulk}}(\partial \phi_{\text{bulk}}/\partial x)$ and $D_{\text{bulk}}$ are the dimensionless current density and the diffusion coefficient in the porous matrix, respectively. $D_{\text{bulk}}$ is different from its bulk value $D$ to account for the tortuosity. The boundary conditions at the macroscopic electrode–solution interface ($x = 0$) require the continuity of the fluxes of every ionic specie, salt concentration, and electric potential. Furthermore, the electric current is constant along all of the circuit (the CAPMIX cell and the external circuit, composed of the external source and the load). The salinity change steps, performed in open circuit ($I_{\text{ext}} = 0$), are done by instantaneously substituting the solution in the spacer, leaving unchanged the solution in a layer close to the electrode of thickness $L_{\text{change}}$. In this work, we arbitrarily set its value to $L_{\text{change}} = 20 \mu$m. A more detailed description of the model and its solution can be found in the original work.$^{16}$ In the present work, we numerically solve the coupled set of eqs 1–6 together with the specified boundary conditions.

## RESULTS AND DISCUSSION

Figure 3 illustrates the nontrivial dynamics, followed by $V_{\text{cell}}$ during the operation of a CDLE cell. As we can see, after the four-step cycle, the cell comes back to its initial state demonstrating the feasibility of the technique. Together with the measured cycle, we have also plotted in Figure 3 the results of the discussed model, and a very good agreement between measurements and the numerical solution of eqs 1–6 is found.

Whereas the charge and discharge steps have been previously analyzed,$^{16}$ the open circuit steps present new phenomenology, with transport mechanisms with different time scales others than salt diffusion. When the solution is changed from saline to fresh water, salt diffuses from the highly concentrated macropores toward the fresh solution, thus establishing a concentration gradient inside the porous matrix and the bulk (quite sharp at short times after the switching, $\tau \equiv L_{\text{change}}/D \lesssim 1$ s, smoothing out on larger time scales). After the fresh-to-saline change, diffusion takes place from the spacer to the macropores. As already observed$^{14,5}$ the time evolution of the cell voltage upon solution change is asymmetric (see Figure 3), as the time needed to stabilize the voltage rise (switch from saline water to fresh water) is much longer than the characteristic fall time (fresh to saline) and also from the characteristic time of the diffusion inside the macropores of the electrode. Here we show that this behavior is mainly due to the highly nonlinear voltage–concentration relation, as shown in Figure 4: when the concentration is above 200 mM, the voltage changes very little with concentration, whereas below that value the dependence is very strong.

Indeed Figure 4 shows the position-dependent path, followed by the cell in the voltage–concentration space. Remarkably, the highest salt concentration $C_{\text{saline}} = 500$ mM is not reached at any point inside the porous matrix. This is due to the nonlinearity of the voltage–concentration dependence, which makes the cell voltage saturate at about $C_{\text{inlet}} = 300$ mM. As the cell is operated in view of the cell voltage, the next step...
Δposition interface, which determines the position the order determined by the arrow: the macroscopic electrode showing the evolution of the cell voltage with the salt concentration at dotted and thick solid lines: simulated CAPMIX cycle in Figure 1, respectively. Circles locate the initial state of each step, starting at open-circuit step, the concentration at pores. In this case, we see that in the saline-to-fresh solution about 400 to 100 mM concentration without any e-flux factors increase the value of the Debye length, covering distances to the surface several times larger than this characteristic size. Furthermore, it has been recently shown that steric effects increase the value of the Debye length. On the other hand, the diffusion inside the micropores in the absence of EDL overlap (seawater) would slow down the dynamics, leading to a more similar characteristic times of the fresh-to-saline and the saline-to-fresh solution change steps. Therefore, although its inclusion is certainly important, it can be neglected in the present study aiming at the identification of the mechanisms responsible of the observed asymmetry.

**CONCLUSIONS**

In summary, we have shown that the used model of the electro-diffusion of ions in porous electrodes is able to describe fairly well the full cyclic process of energy harvesting from salinity gradients with CDLE. The complex evolution of the cell potential observed in experiments has been explained, taking into account the adsorption and desorption of charge and salt into the micropores, the nonlinearity of the charge−voltage relations of the EDLs, and the transport of salt and charge in the electro-neutral macropores of the carbon electrodes. Altogether, these mechanisms lead to nonuniform charge and salt adsorption in the electrodes, considerably affecting the performance of the CAPMIX cell. The model thus validated is a key tool for the optimization of the CDLE technique.

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Notes
The authors declare no competing financial interest.

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