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Charge/discharge of an electrochemical supercapacitor electrode pore; non-uniqueness of mathematical models

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Abstract

A thermodynamic analysis has been done to enhance understanding of the relation between various mathematical models for electrochemical supercapacitor pores. For the same capacitive charge/discharge experiment a variety of one-dimensional mathematical model equations concerning the transport of ions and double layer charge/discharge along the pore are shown to be indistinguishable. Some of those indistinguishable equations could be interpreted as derived from diffusional mechanisms while others appear as derived from migrational mechanisms. Ohmic resistivities and diffusivities obtained in such case are not contradicting results but characterize identical physical processes. The results are valid as long as the assumptions of irreversible thermodynamics of local equilibrium along the pore and of linearization of the flux equations hold.

Keywords: Single pore model; Mathematical model; Irreversible thermodynamics; Ionic diffusion; Ionic migration; Electrochemical supercapacitor

1. Introduction

Electrodes for electrochemical double layer capacitors (EDLCs) or electrochemical supercapacitors typically consist of porous materials such as carbon [1]. The transport properties for ions in the pores are essential for the performance of supercapacitor electrodes [1–6]. Transport parameters may be obtained from dynamic voltammetry experiments, especially potential steps and impedance spectroscopy. Such experiments are commonly evaluated using mathematical models based on principles originating from de Levie's seminal paper from 1963 [1,7] where the main transport resistance is assumed to be the ohmic resistance to ionic migration in the pore electrolyte solution. However, recent work has shown that potential step experiments also may be successfully evaluated using models based on Fickian diffusion of ions in the pores with effective diffusivities as the main transport parameters [5,8–11].

The purpose of this work is to show that there is no contradiction in this situation. Such voltammetry experiments under frequently used experimental conditions cannot give unique information on the transport mechanisms for the ions. The fundamental thermodynamic analysis in this paper shows that for the same experiment a variety of mathematical model equations are equally valid. Some of those equivalently valid equations could be interpreted as derived from diffusional mechanisms while others appear as derived from migrational mechanisms.

2. Model assumptions

2.1. The model pore at equilibrium

We assume a straight cylindrical pore with walls of an electrically conducting material e.g. carbon (see Fig. 1). The pore is filled with a 1,1-electrolyte solution, typically KOH or KF in water. The diameter of the pore is assumed to be substantially greater than twice the Debye

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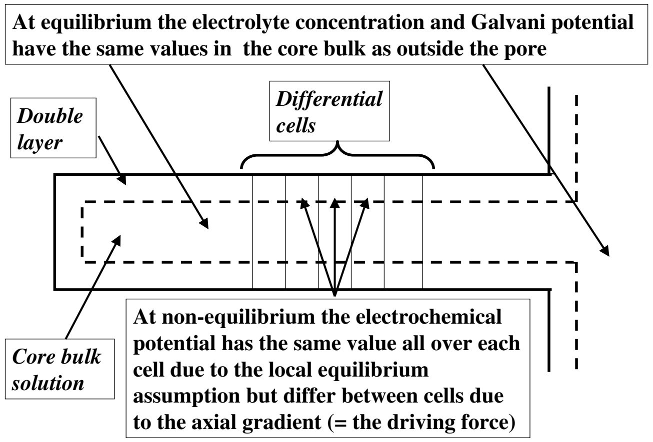

Fig. 1. A schematic picture of a model pore.

length of the electrolyte. As a consequence there is a central part of the pore solution with constant ionic concentrations at equilibrium, while close to the pore wall, within the diffuse part of the double layer, concentrations vary with the radial coordinate. At typical electrolyte concentrations used for electrochemical supercapacitors the diffuse layer is collapsed and only ~0.5 nm in thickness [12]. At equilibrium the Galvani inner potential of the electrolyte is constant within the central core of the pore solution while it varies with the radial coordinate in the diffuse part of the double layer. On the other hand at equilibrium the electrochemical potentials of the ions have the same value everywhere in the system including the diffuse double layer and ions adsorbed on the surface. The values of the Galvani potential, the electrochemical potentials and the concentrations in the central core of the pore and the corresponding values in the external solution outside the pore mouth are equal. The equilibrium relation between Galvani potential and concentrations of ions in the pore is discussed below.

2.2. The model pore during charge/discharge

At non-equilibrium conditions we assume that the driving forces for the flow of ions are the gradients in the electrochemical potentials and that linearized flux equations according to classical irreversible thermodynamics (CIT) are valid (see e.g. [13]), i.e. flux equations like Eq. (16) below (note that Onsager's reciprocal relations are not needed in this work). We assume a one-dimensional case where the gradients in electrochemical potentials have axial directions.

Furthermore we adopt the local equilibrium assumption of CIT. In Fig. 1 differential (infinitesimal) cells along the pore have been illustrated. Local equilibrium assumption means that there is an assumed equilibrium in each cell, however different in different cells, although the whole pore is not in equilibrium. This is a standard postulate in CIT.

The ohmic resistivity of the solid material is assumed negligible.

3. Mathematical model equations

3.1. Transport in the core bulk solution

The following Eq. (1) give the fluxes of the ions in the core bulk electrolyte space. In the first place we assume that only cations are desorbed/adsorbed and transported during charge/discharge i.e. we assume that the transport number for anions equals zero. In that way we obtain a simplest possible example useful for illustrating the principles of the theory. A more general treatise then follows.

Since we assume that the concentration and inner potential are constant over the cross section in this core we obtain a one-dimensional equation. In the first place we assume for simplicity that concentrations are so small that the Nernst–Einstein equation is valid.

$$\begin{aligned} J_{1\mathrm{b}} &= -D_{1\mathrm{b}}\frac{\partial c_{1\mathrm{b}}}{\partial x} - c_{1\mathrm{b}}u_1\frac{\partial \phi}{\partial x} \\ &= -\frac{D_1 c_{1\mathrm{b}}}{RT}\left(\frac{RT}{c_{1\mathrm{b}}}\frac{\partial c_{1\mathrm{b}}}{\partial x} + F\frac{\partial \phi}{\partial x}\right) = -L_{1\mathrm{b}}\frac{\partial \tilde{\mu}_1}{\partial x} \end{aligned} \tag{1}$$

where index 1 refers to cation and index b to core bulk.

Those equations relate the phenomenological coefficients (L_{ik}) of classical irreversible thermodynamics to dilute theory transport equations for very dilute electrolyte solutions. The CIT driving force is the gradient of the electrochemical potential. For higher concentrations the same classical irreversible thermodynamics linearized formulation holds as long as the interaction between cations and anions may be neglected or, as we have assumed, only cations are transported. However, the relation between $L_{1\mathrm{b}}$ and diffusivity seen in Eq. (1) is of course no longer valid.

3.2. Surface-related transport

In the following equation the flux is calculated per the cross sectional pore space. This is the linearized irreversible thermodynamics transport equations for the cations adsorbed in the double layer (in the sense that they reside either adsorbed on the surface or in the diffuse layer) i.e. we assume that the electrochemical potential gradient is the driving force. Transport is taking place only in the axial direction of the pore since the electrochemical potential gradient in the radial direction is assumed to be negligible.

$$J_{1\mathrm{d}} = -L_{1\mathrm{d}}\frac{\partial \tilde{\mu}_1}{\partial x} \tag{2}$$

where index d refers to the double layer.

3.3. Resulting transport equation

We now add the flow of cations in the bulk solution and the surface related flow both calculated per cross sectional area of the pore.

$$J_1 = J_{1\mathrm{b}}\frac{A_\mathrm{b}}{A_\mathrm{pore}} + J_{1\mathrm{d}} = -\left(L_{1\mathrm{b}}\frac{A_\mathrm{b}}{A_\mathrm{pore}} + L_{1\mathrm{d}}\right)\frac{\partial \tilde{\mu}_1}{\partial x} = -L_1\frac{\partial \tilde{\mu}_1}{\partial x} \tag{3}$$