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Abstract Ionic electro-active polymers (E.A.P.) is an active material consisting in a polyelectrolyte (for example Nafion). Such material is usually used as thin film sandwiched between two platinum electrodes. The polymer undergoes large bending motions when an electric field is applied across the thickness. Conversely, a voltage can be detected between both electrodes when the polymer is suddenly bent. The solvent-saturated polymer is fully dissociated, releasing cations of small size. We used a continuous medium approach. The material is modelled by the coexistence of two phases; it can be considered as a porous medium where the deformable solid phase is the polymer backbone with fixed anions; the electrolyte phase is made of a solvent (usually water) with free cations.

The microscale conservation laws of mass, linear momentum and energy and the Maxwell's equations are first written for each phase. The physical quantities linked to the interfaces are deduced. The use of an average technique applied to the two-phase medium finally leads to an Eulerian formulation of the conservation laws of the complete material. Macroscale equations relative to each phase provides exchanges through the interfaces. An analysis of the balance equations of kinetic, potential and internal energy highlights the

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phenomena responsible of the conversion of one kind of energy into another, especially the dissipative ones : viscous frictions and Joule effect.

Keywords Electro-active polymers · balance laws · conservation laws · multiphysics coupling · deformable porous media

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1 Introduction

Electro-active polymers (EAP) have attracted much attention from scientists and engineers of various disciplines. In particular, researches in the field of biomimetics (for instance, in robotic mechanisms are based on biologically-inspired models) and for the use as artificial muscles (see, for instance, the review of Shahinpoor [1] and [2] or [3]) and more recently EAPs are excellent candidates for energy harvesting devices [4], [5] and [6]. Roughly speaking, such polymers have responses to external electric stimulation by displaying a significant shape and size variations. This interesting property offers many promising applications in advanced technologies. In addition, they can be used as actuators or sensors. As actuators the EAPs are characterized by the fact they undergo a large amount of deformation while sustaining large forces. They are often called artificial muscles [7], [8] and [9].
Electro-active polymers can be divided in several categories according to their process of activation and chemical compositions. Nevertheless, they can be placed in two major categories : electronic and ionic categories. These both categories come in several families [3] (among them, ferroelectric polymers, dielectric EAP, electrostrictive paper, electro-viscoelastic elastomers, ionic polymer gels, conductive polymers, etc.). The first category of EAP is the electronic type. Concerning their advantages the E.A.P. can operate in room conditions with rapid response in time; in addition they induce relatively large actuation forces. One of the main disadvantage is that they require high voltage (150 MV/m). The second category, the ionic EAPs, with which the present work is concerned, operates with low voltage (few volts) producing large bending displacements. Their drawbacks are more or less slow response and low actuation force. They operate best in humid environment and they can be made as self-contained encapsulated actuators to be used in dry environment.

In the present study the emphasis is placed especially on the ionic polymer metal composite (IPMC) [10]. The structure consists of thin ion-exchange membrane of Nafion, Flemion or Aciplex (polyelectrolyte) plated on both faces by conductive electrodes (generally platinum or gold). In short, to explain the mechanism of deformation of an EAP, a thin trip of polymers is placed between thin conductive electrodes. Upon the application of an electric field across a slightly humid EAP, the positive counter ions move towards the negative electrode (cathode), whole negative ions that are fixed (or immobile) to

the polymer backbone experience an attractive force from the positive electrode (anode). At the same time, water molecules in the EAP backbone diffuse towards the region of high positive ion concentration (near the negative electrode) to equalize the charge distribution. As a result, the water or solvent concentration in the region near the anode increases and the concentration in the region near the cathode decreases, leading to strain with linear distribution along the step thickness which causes the bending towards the positive anode. Conversely, if the strip of electro-active polymers is suddenly bent, a difference of electric voltage is produced between electrodes [11] and [12].

The theories or models to explain the mechanism of deformation in EAP are yet to emerge. Nevertheless, some heuristic or empiric models are available in the literature. One of the most interesting and comprehensive accounts for chemical mechano-electric effect of the ionic transport coupled to electric field and elastic deformation of the polymer. A micro mechanical model has been developped by Nemat-Nasser [10] and [13] accounting for coupled ion transport, electric field and elastic deformation to predict the response of the IPMC. The model presented is mostly governed by Gauss equation for the conservation of electric charge, a constitutive equation for ion flux vector and a so-called generalized Darcy's law for the water molecule velocity. Other models based on linear irreversible thermodynamics have been proposed by Shahinpoor *et al.* [8] and [14]. The model considers standard Onsager formulation for the simple description of ion transport (current density) and the flux of the solvent transport. The conjugate forces are the electric field and the gradient of pressure. In different way, Shahinpoor and co-workers propose models for micro-electro-mechanics of ions polymeric gels based on continuum electromechanics [7].

The present work focus on a novel approach for electro-active polymers based on thermodynamics of continua. More precisely, we present a detailed approach for such polymer material using the concepts of non-equilibrium thermodynamical processes. The material is then modeled by the coexistence of two phases. The first one is the backbone polymer or the solid phase with fixed anion while the second phase is the solvent containing the free cations. The method consists of computing an average of the different phases over a representative elementary volume containing the phases at the micro scale. The statistical average leads to macro scale quantities defined all over the material. The main difficulty of the method is that we must account for the interfaces which exist between phases for which interfacial quantities must be defined. On using this procedure for different conservation laws of the present multiphase material, we deduce the equation of mass conservation, the electric charge conservation, the conservation of the momentum, the different energy balance equations at the macroscopic scale of the whole material.

The paper is organized as follows. The description of the model and the definition of phases are presented with underlying physics in the next Section.

Section 3 is devoted to the equations of conservation of mass. Since the polymer contains electric charges, the electric charge conservation and interface equations are presented in Section 4. The following Section places the emphasis on the linear momentum balance equation where the macroscopic stress tensor is defined. Moreover, the Maxwell's tensor is placed in evidence due to the action of the electric field on the moving electric charges. The Section 6 presents the energy balance laws, that is, the potential energy, the kinetic energy, the total energy and internal energy balance equations. At last, the discussion is reported in Section 7 and finally conclusions are drawn in Section 8.

2 Modelling

As mentioned in the introduction, the system under study is made of a thin membrane of an ionic electro-active polymer saturated with water and coated on both sides with thin metal layers used as electrodes. Water, even in small quantity, causes a quasi-complete dissociation of the polymer and the release of positive ions (cations) in water; negative ions (anions) remain bound to the polymer backbone [15]. When an electric field perpendicular to the electrodes is applied, cations move towards the negative side, carrying solvent away by an osmosis phenomenon. This solvent displacement leads to a polymer swelling on the negative electrode side and to a compression on the opposite side, resulting in a bending of the strip.

To model this system, we describe the polymer chains as a deformable porous medium; this solid is saturated by an ionic solution composed by water and cations. The whole material is considered as a continuum, which is the superposition of three systems whose velocity fields are different : a deformable solid component made up of polymer backbone negatively charged and fluid trapped in the unconnected porosity (the "solid component"), and a liquid composed of water and cations located in the connected porosity. Anions are bound to the solid component. Quantities relative to the different components will be respectively identified by subscripts 1, 2 and 3 for cations, solvent and solid. Subscript 4 will refer to the solution, i.e. both components 1 and 2. Quantities without subscript refer to the whole material. Solid and solution are separated by an interface (subscript i) whose thickness is supposed to be negligible. Components 2, 3 and 4 as well as the global material are assimilated to continua. Modelling of the interface is detailed in the appendix.

Solid and solution are supposed to be incompressible phases. We assume the gravity and the magnetic field are negligible; the only external force acting on the system is the electric force.

To describe this complex dispersed medium, we use a coarse-grained model developed by Nigmatulin [16], [17], Drew [18], Drew and Passman [19] and Ishii and Hibiki [20] for two-phase mixtures [21]. We use two scales. The microscopic scale must be small enough so that the corresponding volume only contains a single phase (3 or 4), but large enough to use a continuous medium model. For

Nafion completely saturated with water, it is about hundred Angstroms. At the macroscopic scale, the representative elementary volume (R.E.V.) contains phases 3 and 4. It must be large enough so that average quantities relative to the whole material make sense, and small enough so that these quantities can be considered as local. Its characteristic length is about micron [22], [23] and [15]. For each phase 3 and 4, we define a microscale Heaviside-like function of presence $\chi_k(\overrightarrow{r}, t)$ by

$$\chi_k = 1 \text{ when phase } k \text{ occupies point } \overrightarrow{r} \text{ at time t}, \quad \chi_k = 0 \text{ otherwise} \quad (1)$$

χ_k remains unchanged in case of displacement following the interface velocity $\overrightarrow{V_i^0}$. We obtain

$$\overrightarrow{grad}\chi_k = -\overrightarrow{n_k}\chi_i \qquad \frac{\partial \chi_k}{\partial t} = \overrightarrow{V_i^0} \cdot \overrightarrow{n_k}\chi_i \qquad \text{for } k = 3, 4 \qquad (2)$$

where the Dirac-like function $\chi_i = -\overrightarrow{grad}\chi_k \cdot \overrightarrow{n_k}$ (in m^{-1}) denotes the function of presence of the interface and $\overrightarrow{n_k}$ the outward-pointing unit normal to the interface in the phase k.

The quantities related to each phase have significant variation over space and time, as well as the positions of each phase. In order to define macroscale quantities relative to the whole material, we consider a representative elementary volume (R.E.V.) containing the three components and the microscale quantities are statistically averaged over the R.E.V.. This statistical average, denoted by $\langle \rangle$ and obtained by repeating many times the same experiment with the same boundary and initial conditions, is supposed to be equivalent to a volume average (ergodic hypothesis). The average thus defined commutes with the space and time derivatives (Leibniz' and Gauss' rules, Drew [18]; Lhuillier [21]). On denoting by $\langle \rangle_k$ the average over the phase k of a quantity relative to the phase k only, a microscale quantity g_k^0 satisfies

$$g_k = \left\langle \chi_k g_k^0 \right\rangle = \phi_k \left\langle g_k^0 \right\rangle_k \qquad (3)$$

where $\phi_k = \langle \chi_k \rangle$ is the volume fraction of the phase k. The macroscale quantity g_k is defined all over the material. In the following, superscript ^{0} denotes the microscale quantities of each phase. The macroscale quantities, which are averages defined everywhere, are written without superscript.

3 Equation of conservation of mass

In the following, we assume that the polymer is enough hydrated to be completely dissociated. For the water, solution and solid phases, the microscale mass continuity equation can be written as

$$\frac{\partial \rho_k^0}{\partial t} + div\left(\rho_k^0 \overrightarrow{V_k^0}\right) = 0 \qquad (4)$$

where $\overrightarrow{V_k^0}$ is the local velocity of the phase k and ρ_k^0 its mass density. Phases 2 and 3 are incompressible, so we obtain

$$div\left(\overrightarrow{V_k^0}\right) = 0 \tag{5}$$

The different phases do not interpenetrate, thus we can write

$$\overrightarrow{V_1^0}\chi_i = \overrightarrow{V_2^0}\chi_i = \overrightarrow{V_3^0}\chi_i = \overrightarrow{V_4^0}\chi_i = \overrightarrow{V_i^0}\chi_i \tag{6}$$

Using (4) and (2) we deduce

$$\frac{\partial\chi_k\rho_k^0}{\partial t} + div\left(\chi_k\rho_k^0\overrightarrow{V_k^0}\right) = \rho_k^0\overrightarrow{V_i^0}\cdot\overrightarrow{n_k}\chi_i - \rho_k^0\overrightarrow{V_k^0}\cdot\overrightarrow{n_k}\chi_i \tag{7}$$

For the phase k, the mass density relative to the whole material volume and the barycentric velocity are defined respectively by

$$\rho_k = \left\langle\chi_k\rho_k^0\right\rangle = \phi_k\rho_k^0 \qquad \overrightarrow{V_k} = \frac{\left\langle\chi_k\rho_k^0\overrightarrow{V_k^0}\right\rangle}{\left\langle\chi_k\rho_k^0\right\rangle} = \overrightarrow{V_k^0} \tag{8}$$

neglecting the velocities fluctuations on the R.E.V. scale.

$$\rho_4^0 = \rho_2^0\frac{\phi_2}{\phi_4} + CM_1 \tag{9}$$

where M_k is the molar mass of the component k and C the cations molar concentration relative to the solution volume. It follows

$$\rho_4 = \rho_1 + \rho_2 \qquad \text{with} \qquad \rho_1 = \phi_4 CM_1 \tag{10}$$

assuming that the concentration fluctuations are negligible and that the solution is diluted. In the same way the velocity of the solution can be written as

$$\rho_4^0\overrightarrow{V_4^0} = CM_1\overrightarrow{V_1^0} + \rho_2^0\frac{\phi_2}{\phi_4}\overrightarrow{V_2^0} \qquad \rho_4\overrightarrow{V_4} = \rho_1\overrightarrow{V_1} + \rho_2\overrightarrow{V_2} \tag{11}$$

Averaging over the material R.E.V., we finally obtain

$$\frac{\partial\rho_k}{\partial t} + div\left(\rho_k\overrightarrow{V_k}\right) = 0 \qquad k = 1, 2, 3, 4 \tag{12}$$

The interfaces have no mass. Consequently, we deduce for the complete material

$$\frac{\partial\rho}{\partial t} + div\left(\rho\overrightarrow{V}\right) = 0 \tag{13}$$

where ρ and $\overrightarrow{V}$ denote the mass density and the barycentric velocity of the whole material

$$\rho = \sum_{k=3,4}\rho_k \qquad \rho\overrightarrow{V} = \sum_{k=3,4}\rho_k\overrightarrow{V_k} \tag{14}$$

4 Electric equations

4.1 Electric charge conservation

The microscale electric charge conservation of the phase k can be written

$$div\overrightarrow{I_k^0} + \frac{\partial \left(\rho_k^0 Z_k^0\right)}{\partial t} = 0 \tag{15}$$

where $\overrightarrow{I_k^0}$ denotes the current density vector and Z_k^0 the electric charge per unit of mass (Z_2^0 and Z_3^0 are constants).

$$\overrightarrow{I_3^0} = \rho_3^0 Z_3^0 \overrightarrow{V_3^0} \qquad\qquad \overrightarrow{I_4^0} = M_1 C Z_1^0 \overrightarrow{V_1^0} \tag{16}$$

$$Z_k^0 = \frac{z_k F}{M_k} \qquad \text{for} \quad k = 1,3 \qquad Z_2^0 = 0 \qquad Z_4^0 = \frac{C M_1 Z_1^0}{\rho_4^0} \tag{17}$$

where z_k is the number of elementary charges of an ion and F the Faraday's constant.

Averaging over the R.E.V., we obtain

$$div\overrightarrow{I_k} + \frac{\partial \rho_k Z_k}{\partial t} = \left\langle -\overrightarrow{i_k^0} \cdot \overrightarrow{n_k} \chi_i \right\rangle \tag{18}$$

in which the macroscale mass charge and current density vector are defined as

$$\rho_k Z_k = \left\langle \chi_k \rho_k^0 Z_k^0 \right\rangle \qquad\qquad \overrightarrow{I_k} = \left\langle \chi_k \overrightarrow{I_k^0} \right\rangle \tag{19}$$

with

$$\overrightarrow{I_3} = \left\langle \chi_3 \overrightarrow{I_3^0} \right\rangle = \rho_3 Z_3 \overrightarrow{V_3} \qquad\qquad \overrightarrow{I_4} = \left\langle \chi_4 \overrightarrow{I_4^0} \right\rangle = \rho_1 Z_1 \overrightarrow{V_1} \tag{20}$$

$\overrightarrow{i_k^0} = \overrightarrow{I_k^0} - \rho_k^0 Z_k^0 \overrightarrow{V_k^0}$ denotes the microscale diffusion current in phase k. Quantities relative to the interfaces are defined in the appendix. The interface electric charge density per unit surface Z_i and the current density vector $\overrightarrow{I_i}$ satisfy the following mean condition

$$\frac{\partial Z_i}{\partial t} + div\overrightarrow{I_i} = \left\langle \overrightarrow{i_3^0} \cdot \overrightarrow{n_3} \chi_i + \overrightarrow{i_4^0} \cdot \overrightarrow{n_4} \chi_i \right\rangle \tag{21}$$

Adding up equations (18) for the solid, the solution and (21) for the interfaces, it follows for the whole material

$$div\overrightarrow{I} + \frac{\partial \rho Z}{\partial t} = 0 \tag{22}$$

where

$$\rho Z = \sum_{3,4} \rho_k Z_k + Z_i \qquad\qquad \overrightarrow{I} = \rho_1 Z_1 \overrightarrow{V_1} + \rho_3 Z_3 \overrightarrow{V_3} + \overrightarrow{I_i} \tag{23}$$

4.2 Maxwell's equations

One can reasonably neglect the effects of the magnetic field. The electric fields $\overrightarrow{E_k^0}$ and the electric displacements $\overrightarrow{D_k^0}$ of the solid and the solution are governed by the Maxwell's equations

$$\overrightarrow{rot}\,\overrightarrow{E_k^0} = \overrightarrow{0} \qquad\qquad div\,\overrightarrow{D_k^0} = \rho_k^0 Z_k^0 \qquad\qquad (24)$$

The associated boundary conditions can be presented as

$$\overrightarrow{n_3} \wedge \overrightarrow{E_3^0}\chi_i = -\overrightarrow{n_4} \wedge \overrightarrow{E_4^0}\chi_i \qquad\qquad \overrightarrow{D_3^0} \cdot \overrightarrow{n_3}\chi_i + \overrightarrow{D_4^0} \cdot \overrightarrow{n_4}\chi_i + Z_i^0\chi_i = 0 \quad (25)$$

Averaging equations (24) over the R.E.V., we derive the following macroscale equations for the solid and the solution

$$\overrightarrow{rot}\,\overrightarrow{E_k} = \overrightarrow{0} \qquad\qquad div\,\overrightarrow{D_k} = \rho_k Z_k - \left\langle \overrightarrow{D_k^0} \cdot \overrightarrow{n_k}\chi_i \right\rangle \qquad\qquad (26)$$

in which the macroscale electric fields and displacements are defined as

$$\overrightarrow{E_k} = \frac{\left\langle \chi_k \overrightarrow{E_k^0} \right\rangle}{\langle \chi_k \rangle} \qquad\qquad \overrightarrow{D_k} = \left\langle \chi_k \overrightarrow{D_k^0} \right\rangle \qquad\qquad (27)$$

Electric field is an intensive thermodynamic variable. In principle, it displays spatial and time fluctuations within the R.E.V.. Considering this volume is tiny, we assume that the fluctuations are not relevant; we venture the same hypothesis for the concentration and the velocities of the phases. Furthermore, we suppose that macroscale electric fields are identical in all the phases. Adding up equations (26) for the solid and the solution, it follows for the whole material

$$\overrightarrow{rot}\,\overrightarrow{E} = \overrightarrow{0} \qquad\qquad div\,\overrightarrow{D} = \rho Z \qquad\qquad (28)$$

using (25). Parameters of the complete material are defined by

$$\overrightarrow{E} = \sum_{3,4} \phi_k \overrightarrow{E_k} = \overrightarrow{E_k} \qquad\qquad \overrightarrow{D} = \sum_{3,4} \overrightarrow{D_k} \qquad\qquad (29)$$

We conclude that the E.A.P. verifies the same Maxwell's equations and the same law of conservation of charge as an isotropic homogeneous linear dielectric.

4.3 Constitutive relations

A reasonable approximation is that solid and solution can be regarded as isotropic linear dielectrics

$$\overrightarrow{D_k^0} = \varepsilon_k^0 \overrightarrow{E_k^0} \qquad\qquad (30)$$

where ε_k^0 denotes the permittivity of the phase k. Average over the R.E.V. gives

$$\overrightarrow{D_k} = \varepsilon_k \overrightarrow{E_k} \tag{31}$$

in which :

$$\varepsilon_k = \left\langle \chi_k \varepsilon_k^0 \right\rangle \tag{32}$$

is the mean permeability of the phase k relative to the total volume.

The constitutive relation of the E.A.P. takes on the following form

$$\overrightarrow{D} = \varepsilon \overrightarrow{E} \tag{33}$$

where the whole material permittivity is defined by

$$\varepsilon = \sum_{k=3,4} \varepsilon_k \tag{34}$$

On considering our assumptions, the E.A.P. is equivalent to an isotropic linear dielectric. We however point out that its permittivity a priori varies over time and space because of variations of the volume fractions ϕ_3 and ϕ_4.

5 Linear momentum conservation law

5.1 Particle derivatives and material derivative

In order to write the remaining balance equations, it is necessary to calculate the variations of the extensive quantities following the material motion. This raises a problem because the different phases do not move with the same velocity : velocities of the solid and the solution are a priori different. For a quantity g, we can define particle derivatives following the motion of the solid $\left(\frac{d_3}{dt}\right)$, the solution $\left(\frac{d_4}{dt}\right)$ or the interface $\left(\frac{d_i}{dt}\right)$

$$\frac{d_k g}{dt} = \frac{\partial g}{\partial t} + \overrightarrow{grad}g \cdot \overrightarrow{V_k} \tag{35}$$

Let us consider an extensive quantity of density $g\left(\overrightarrow{r}, t\right)$ relative to the whole material. According to the theory developped by O. Coussy [24] and implicitly used in [25] and [26], we are able to define a derivative following the motion of the different phases of the medium. We will call it the "material derivative"

$$\frac{D}{Dt}\left(\frac{g}{\rho}\right) = \sum_{k=3,4,i} \frac{\rho_k}{\rho} \frac{d_k \left(\frac{g_k}{\rho_k}\right)}{dt} \tag{36}$$

where g_3, g_4 and g_i are the densities relative to the total actual volume attached to the solid, the solution and the interface, respectively (for example, if g is the volume density, we set $g_3 = 1 - \phi$ and $g_4 = \phi$ where ϕ is the porosity)

$$g = g_3 + g_4 + g_i \tag{37}$$

$\frac{d_k}{dt}\left(\frac{g_k}{\rho_k}\right)$ is the derivative following the motion of the phase k of the mass density associated with the quantity g_k. Using (12), we derive

$$\rho\frac{D\left(\frac{g}{\rho}\right)}{Dt} = \sum_{k=3,4,i} \frac{\partial g_k}{\partial t} + div\left(g_k\overrightarrow{V_k}\right) \tag{38}$$

for a scalar quantity and

$$\rho\frac{D\left(\frac{\overrightarrow{g}}{\rho}\right)}{Dt} = \sum_{k=3,4,i} \frac{\partial \overrightarrow{g_k}}{\partial t} + \overrightarrow{div}\left(\overrightarrow{g_k} \otimes \overrightarrow{V_k}\right) \tag{39}$$

for a vector quantity. This derivative must not be confused with the derivative $\frac{d}{dt}$ following the barycentric velocity $\overrightarrow{V}$.

5.2 Linear momentum balance equation

On assuming that the gravity and the magnetic field are negligible, the only applied volume force is the electric one. The microscale momentum balance equation of the phase k is then written as

$$\frac{\partial \rho_k^0 \overrightarrow{V_k^0}}{\partial t} + \overrightarrow{div}\left(\rho_k^0 \overrightarrow{V_k^0} \otimes \overrightarrow{V_k^0}\right) = \overrightarrow{div}\underline{\sigma}_k^0 + \rho_k^0 Z_k^0 \overrightarrow{E_k^0} \tag{40}$$

where $\underline{\sigma}_k^0$, the microscale stress tensor of the phase k, is symmetric. The linear momentum of the interfaces per surface unit is zero (see appendix). On accounting for the assumptions concerning the local velocities, it follows that at the macroscopic scale

$$\frac{\partial \rho_k \overrightarrow{V_k}}{\partial t} + \overrightarrow{div}\left(\rho_k \overrightarrow{V_k} \otimes \overrightarrow{V_k}\right) = \overrightarrow{div}\underline{\sigma}_k + \rho_k Z_k \overrightarrow{E_k} + \overrightarrow{F_k} \tag{41}$$

where

$$\underline{\sigma}_k = \left\langle \chi_k \underline{\sigma}_k^0 \right\rangle \qquad \overrightarrow{F_k} = \left\langle \underline{\sigma}_k^0 \cdot \overrightarrow{n_k}\chi_i \right\rangle \tag{42}$$

We verify that the macroscale stress tensor of the phase k, $\underline{\sigma}_k$, is symmetric. $\overrightarrow{F_k}$ represents the resultant of the mechanical stresses exerted on the phase k by the other phase; it is an interaction force. Concerning the interfaces, we obtain the following mean condition (cf § 9), which expresses the linear momentum conservation law for the interfaces

$$\overrightarrow{F_3} + \overrightarrow{F_4} = Z_i\overrightarrow{E_i} \tag{43}$$

The interface momentum is zero, then the volume linear momentum of the whole material is $\rho\overrightarrow{V} = \rho_3\overrightarrow{V_3} + \rho_4\overrightarrow{V_4}$. On using the definition of the material derivative (39), we obtain

$$\rho\frac{D\overrightarrow{V}}{Dt} = \overrightarrow{div}\underset{\sim}{\sigma} + \rho Z\overrightarrow{E} \tag{44}$$

in which

$$\underset{\sim}{\sigma} = \sum_{k=3,4} \sigma_k \tag{45}$$

We check that $\underset{\sim}{\sigma}$ is a symmetric tensor and that in the absence of any external force $(\overrightarrow{E} = \overrightarrow{0})$, the total linear momentum is conserved.

Using Maxwell's equations (28) and (33), (44) becomes

$$\rho\frac{D\overrightarrow{V}}{Dt} = \overrightarrow{div}\left[\underset{\sim}{\sigma} + \varepsilon\left(\overrightarrow{E} \otimes \overrightarrow{E} - \frac{E^2}{2}\underset{\sim}{I}\right)\right] + \frac{E^2}{2}\overrightarrow{grad}\varepsilon \tag{46}$$

$\varepsilon\left(\overrightarrow{E} \otimes \overrightarrow{E} - \frac{E^2}{2}\underset{\sim}{I}\right)$ is the Maxwell's tensor, which is here symmetric. The additional term $\frac{E^2}{2}\overrightarrow{grad}\varepsilon$ is produced by the non homogeneous material permittivity.

6 Energy balance laws

6.1 Potential energy balance equation

Solid and solution are supposed to be non-dissipative isotropic linear media. As a consequence the balance equation for the potential energy or Poynting's theorem can be written in the integral form [27], [28]

$$\frac{d}{dt}\int_\Omega \frac{1}{2}\left(\overrightarrow{E} \cdot \overrightarrow{D} + \overrightarrow{B} \cdot \overrightarrow{H}\right) dv = -\oint_{\partial\Omega}\left(\overrightarrow{E} \wedge \overrightarrow{H}\right) \cdot \overrightarrow{n}\, ds - \int_\Omega \overrightarrow{E} \cdot \overrightarrow{I}\, dv \tag{47}$$

assuming that no charge goes out of the volume Ω. The left hand side represents the variation of the potential energy attached to the volume Ω following the charge motion. If the charges are mobile, the associated local equation writes for the phase k, neglecting the magnetic field

$$\frac{\partial E_{pk}^0}{\partial t} + div\left(E_{pk}^0\overrightarrow{V_k^0}\right) = -\overrightarrow{E_k^0} \cdot \overrightarrow{I_k^0} \qquad k = 3, 4 \tag{48}$$

in which

$$E_{pk}^0 = \frac{1}{2}\overrightarrow{D_k^0} \cdot \overrightarrow{E_k^0} \qquad k = 3, 4 \tag{49}$$

is the potential energy per unit of volume of the phase k. On taking the statistical average of (48) over the R.E.V., we obtain

$$\frac{\partial E_{pk}}{\partial t} + div\left(E_{pk}\overrightarrow{V_k}\right) = -\overrightarrow{E_k} \cdot \overrightarrow{I_k} \tag{50}$$

where

$$E_{pk} = \left\langle \chi_k E_{pk}^0 \right\rangle = \frac{1}{2}\overrightarrow{D_k} \cdot \overrightarrow{E_k} \tag{51}$$

The mean volume potential energy associated to the interfaces satisfies (see appendix)

$$\frac{\partial E_{pi}}{\partial t} + div\left(E_{pi}\overrightarrow{V_i}\right) = -\overrightarrow{E_i} \cdot \overrightarrow{I_i} \tag{52}$$

The potential energy balance equation for the whole material is then

$$\rho\frac{D}{Dt}\left(\frac{E_p}{\rho}\right) = -\overrightarrow{E} \cdot \overrightarrow{I} \tag{53}$$

where

$$E_p = \sum_{3,4,i} E_{pi} = \frac{1}{2}\overrightarrow{D} \cdot \overrightarrow{E} \tag{54}$$

The production of potential energy in the R.E.V. is equal to the volume power $-\overrightarrow{E} \cdot \overrightarrow{I}$ of the force due to the action of the electric field on the density of electric charges.

6.2 Kinetic energy balance equation

The microscale kinetic energy balance equation derives from (40)

$$\frac{\partial E_{ck}^0}{\partial t} + div\left(E_{ck}^0\overrightarrow{V_k^0}\right) = div\left(\underline{\sigma}_k^0\overrightarrow{V_k^0}\right) - \underline{\sigma}_k^0 : \overrightarrow{grad V_k^0} + \rho_k^0 Z_k^0 \overrightarrow{E_k^0} \cdot \overrightarrow{V_k^0} \tag{55}$$

where the microscale volume kinetic energy of the phase k is

$$E_{ck}^0 = \frac{1}{2}\rho_k^0 V_k^{02} \tag{56}$$

In the same way, (41) is transformed into

$$\frac{\partial E_{ck}}{\partial t} + div\left(E_{ck}\overrightarrow{V_k}\right) = \overrightarrow{V_k} \cdot \overrightarrow{div\underline{\sigma}_k} + \rho_k Z_k \overrightarrow{V_k} \cdot \overrightarrow{E_k} + \overrightarrow{F_k} \cdot \overrightarrow{V_k} \tag{57}$$

where

$$E_{ck} = \frac{1}{2}\rho_k V_k^2 \tag{58}$$

is the macroscale volume kinetic energy of the phase k. The interface kinetic energy is zero (see appendix).

On summing up the equations (57) for phases 3 and 4, we arrive at

$$
\begin{aligned}
\rho \frac{D}{Dt}\left(\frac{E_{c\Sigma}}{\rho}\right) \quad &= \sum_{3,4}\left[\frac{\partial E_{ck}}{\partial t} + div\left(E_{ck}\overrightarrow{V_k}\right)\right] \\
&= \sum_{3,4}\left[div\left(\underline{\underline{\sigma}}_k \cdot \overrightarrow{V_k}\right) - \underline{\underline{\sigma}}_k : \underrightarrow{grad\,V_k}\right] + \left[\sum_{3,4}\rho_k Z_k \overrightarrow{V_k} + Z_i\overrightarrow{V_i}\right]\cdot\overrightarrow{E}
\end{aligned}
\tag{59}
$$

where $E_{c\Sigma}$ is the sum of the volume kinetic energies of the different phases with respect to the laboratory reference frame

$$
E_{c\Sigma} = E_{c3} + E_{c4}
\tag{60}
$$

$E_{c\Sigma}$ is distinct from the kinetic energy of the whole material because the phase velocities are different. The total volume kinetic energy E_c is defined as

$$
E_c = \frac{1}{2}\rho V^2 = \sum_{3,4}\frac{1}{2}\rho_k V^2
\tag{61}
$$

From (38), we deduce

$$
\rho\frac{D}{Dt}\left(\frac{E_c}{\rho}\right) = \frac{\partial E_c}{\partial t} + div\left(E_c\overrightarrow{V}\right)
\tag{62}
$$

Using (59), it follows

$$
\begin{aligned}
\rho\frac{D}{Dt}\left(\frac{E_c}{\rho}\right) = &\frac{\partial}{\partial t}\left(E_c - \sum_{3,4}E_{ck}\right) + div\left[\sum_{3,4}\left(\underline{\underline{\sigma}}_k\cdot\overrightarrow{V_k} - E_{ck}\overrightarrow{V_k}\right) + E_c\overrightarrow{V}\right] \\
&- \sum_{3,4}\underline{\underline{\sigma}}_k : \underrightarrow{grad\,V_k} + \left(\sum_{3,4}\rho_k Z_k\overrightarrow{V_k} + Z_i\overrightarrow{V_i}\right)\cdot\overrightarrow{E}
\end{aligned}
\tag{63}
$$

The last two terms of this equation are source terms. The penultimate one represents the viscous dissipation, that is to say kinetic energy conversion into internal energy. The last term is the electric force volume power, which corresponds to a potential energy conversion into kinetic energy. As for the first two terms, they correspond to the kinetic energy flux, which is both due to the contact forces work $\sum_{3,4} div\left(\underline{\underline{\sigma}}_k \cdot \overrightarrow{V_k}\right)$ and to the relative velocity of the two phases: the kinetic energy of the phases with respect to the barycentric reference frame becomes indeed part of the internal energy of the whole material.

6.3 Total energy conservation law

The total energy of the present system is the sum of its internal, potential and kinetic energies. The energy fluxes come from contact forces work and heat

conduction. The microscale energy conservation law for the phase k can be written as

$$\frac{\partial E_k^0}{\partial t} + div\left[E_k^0\overrightarrow{V_k^0} - \underline{\sigma}_k^0 \cdot \overrightarrow{V_k^0} + \overrightarrow{Q_k^0}\right] = 0 \qquad (64)$$

where

$$E_k^0 = U_k^0 + \frac{1}{2}\rho_k^0 V_k^{02} + \frac{1}{2}\overrightarrow{E_k^0} \cdot \overrightarrow{D_k^0} \qquad (65)$$

is the total microscale energy of the phase k. $\overrightarrow{Q_k^0}$ denotes the microscale heat flux of the phase k and U_k^0 its microscale internal energy. Average over the R.E.V. leads to

$$\frac{\partial E_k}{\partial t} + div\left(E_k\overrightarrow{V_k}\right) - div\left(\underline{\sigma}_k \cdot \overrightarrow{V_k}\right) + div\overrightarrow{Q_k} = \overrightarrow{F_k} \cdot \overrightarrow{V_k} + P_k \qquad (66)$$

where

$$E_k = \left\langle \chi_k E_k^0 \right\rangle = U_k + E_{ck} + E_{pk} \qquad U_k = \left\langle \chi_k U_k^0 \right\rangle \qquad \overrightarrow{Q_k} = \left\langle \chi_k \overrightarrow{Q_k^0} \right\rangle \qquad (67)$$

and

$$P_k = \left\langle -\overrightarrow{Q_k^0} \cdot \overrightarrow{n_k}\chi_i \right\rangle \qquad (68)$$

$\overrightarrow{F_k} \cdot \overrightarrow{V_k} + P_k$ represents the energy exchanges between the different phases through the interfaces : contact forces work and heat fluxes. We obtain the following condition for the interfaces (see appendix)

$$\frac{\partial E_i}{\partial t} + div\left(E_i\overrightarrow{V_i}\right) = -P_3 - P_4 - \overrightarrow{F_3} \cdot \overrightarrow{V_3} - \overrightarrow{F_4} \cdot \overrightarrow{V_4} \qquad (69)$$

where E_i is the total energy density of the interfaces averaged over the R.E.V.. On summing equations (66) for $k = 3, 4$ and (69), we obtain the conservation law of the total volume energy of the whole material E

$$\rho\frac{D}{Dt}\left(\frac{E}{\rho}\right) = div\left(\sum_{k=3,4} \underline{\sigma}_k \cdot \overrightarrow{V_k}\right) - div\overrightarrow{Q} \qquad (70)$$

where

$$E = \sum_{3,4,i} E_k = U + E_c + E_p \qquad \overrightarrow{Q} = \sum_{k=3,4} \overrightarrow{Q_k} \qquad (71)$$

The source term of this equation is zero, which is the expression of the conservation law of the energy. $\sum_{3,4} \underline{\sigma}_k \cdot \overrightarrow{V_k}$ and $\overrightarrow{Q}$ represent the volume power of the contact forces and the heat fluxes of the complete medium, respectively.

6.4 Internal energy balance equation

The internal energy equation is obtained by subtracting kinetic and potential energy equations (55) and (48) from the total energy conservation law (64)

$$\frac{\partial U_k^0}{\partial t} + div\left(U_k^0\overrightarrow{V_k^0} + \overrightarrow{Q_k^0}\right) = \underline{\sigma}_k^0 : \underline{grad}\overrightarrow{V_k^0} + \left(\overrightarrow{I_k^0} - \rho_k^0 Z_k^0 \overrightarrow{V_k^0}\right) \cdot \overrightarrow{E_k^0} \qquad (72)$$

Algebraic manipulations of (66), (57) and (50) lead to

$$\frac{\partial U_k}{\partial t} + div\left(U_k\overrightarrow{V_k} + \overrightarrow{Q_k}\right) = \underline{\sigma}_k : \underline{grad}\overrightarrow{V_k} + \overrightarrow{i_k} \cdot \overrightarrow{E_k} - \left\langle \overrightarrow{Q_k^0} \cdot \overrightarrow{n_k}\chi_i \right\rangle \qquad (73)$$

and for the interfaces (see appendix)

$$\frac{\partial U_i}{\partial t} + div\left(U_i\overrightarrow{V_i}\right) = \left\langle \overrightarrow{Q_3^0} \cdot \overrightarrow{n_3}\chi_i + \overrightarrow{Q_4^0} \cdot \overrightarrow{n_4}\chi_i \right\rangle - \overrightarrow{i_i} \cdot \overrightarrow{E_i} \qquad (74)$$

where U_i denotes the volume internal energy of interfaces included in the R.E.V..

Let us define U_Σ as the sum of the volume internal energies of the different phases

$$U_\Sigma = U_3 + U_4 + U_i \qquad (75)$$

From (38), we derive

$$\rho\frac{D}{Dt}\left(\frac{U_\Sigma}{\rho}\right) = \sum_{3,4}\left(\underline{\sigma}_k : \underline{grad}\overrightarrow{V_k}\right) + \overrightarrow{i} \cdot \overrightarrow{E} - div\overrightarrow{Q} \qquad (76)$$

where $\overrightarrow{i}$ represents the diffusion current, consisting of the diffusion currents of the interfaces and of the cations in the solution

$$\overrightarrow{i} = \overrightarrow{I} - \sum_{k=3,4}\left(\rho_k Z_k \overrightarrow{V_k}\right) - Z_i\overrightarrow{V_i} = \rho_1 Z_1\left(\overrightarrow{V_1} - \overrightarrow{V_4}\right) + \overrightarrow{i_i} \qquad (77)$$

U_Σ represents only a part of the internal energy of the whole material; another part comes from the motion of the different phases in the barycentric reference frame. The internal energy of the whole material is defined by

$$U = E - E_c - E_p = U_\Sigma + E_{c\Sigma} - E_c \qquad (78)$$

One deduces

$$\rho\frac{D}{Dt}\left(\frac{U}{\rho}\right) = div\left(\sum_{3,4}E_{ck}\overrightarrow{V_k} - E_c\overrightarrow{V}\right) + \frac{\partial}{\partial t}\left(\sum_{3,4}E_{ck} - E_c\right) - div\overrightarrow{Q}$$
$$+ \sum_{3,4}\left(\underline{\sigma}_k : \underline{grad}\overrightarrow{V_k}\right) + \overrightarrow{i} \cdot \overrightarrow{E} \qquad (79)$$

The first two terms in the right-hand side represent the volume internal energy flux due to the relative velocities of the phases. The fourth one is the volume kinetic energy converted into heat by viscous dissipation. And the last term is the volume heat source by Joule effect in the solution.

7 Discussion

The conservation laws obtained for the global material include simplest cases. Assuming that the material is not electrically charged or removing the electric field, we obtain the equations governing a single-phase flow in porous medium [24]. In case that the stress tensor is zero and that the velocities of the two phases are identical and uniform, we find the equations of a charged rigid solid subjected to an electric field.

The balance equations of the kinetic, potential, internal and total energies all have the same structure : the energy variation following the motion of one constituent, which is a particle derivative, is the sum of a flux and of source terms. The equations we write are relative to a thermodynamic closed system because of the use of the material derivative. Source terms correspond to conversion of one kind of energy into another one. At the microscopic scale, we obtain the following tables for the phase k

$$
\begin{array}{c|c}
 & \text{flux} \\
\hline
E_{pk}^0 & \\
E_{ck}^0 & div\left(\underaccent{\tilde}{\sigma}_k^0 \cdot \overrightarrow{V_k^0}\right) \\
U_k^0 & -div\overrightarrow{Q_k^0} \\
E_k^0 & div\left(\underaccent{\tilde}{\sigma}_k^0 \cdot \overrightarrow{V_k^0} - \overrightarrow{Q_k^0}\right)
\end{array}
\tag{80}
$$

and

$$
\begin{array}{c|c|c|c}
 & E_c \longleftrightarrow E_p & U \longleftrightarrow E_p & E_c \longleftrightarrow U \\
\hline
E_{pk}^0 & -\rho_k^0 Z_k^0 \overrightarrow{E_k^0} \cdot \overrightarrow{V_k^0} & -\left(\overrightarrow{I_k^0} - \rho_k^0 Z_k^0 \overrightarrow{V_k^0}\right) \cdot \overrightarrow{E_k^0} & \\
E_{ck}^0 & +\rho_k^0 Z_k^0 \overrightarrow{E_k^0} \cdot \overrightarrow{V_k^0} & & -\underaccent{\tilde}{\sigma}_k^0 : \underaccent{\tilde}{grad}\overrightarrow{V_k^0} \\
U_k^0 & & +\left(\overrightarrow{I_k^0} - \rho_k^0 Z_k^0 \overrightarrow{V_k^0}\right) \cdot \overrightarrow{E_k^0} & +\underaccent{\tilde}{\sigma}_k^0 : \underaccent{\tilde}{grad}\overrightarrow{V_k^0} \\
E_k^0 & & &
\end{array}
\tag{81}
$$

Fluxes can be considered as the rate of variation of the quantity associated with the conduction phenomenon. The flux of kinetic energy is due to the contact force work, and the flux of internal energy to the heat conduction. The total energy flux is then the sum of the two previous ones. We point out that there is no flux for the potential energy. The viscous dissipation $\underaccent{\tilde}{\sigma}_k^0 : \underaccent{\tilde}{grad}\overrightarrow{V_k^0}$ transforms the kinetic energy into heat, that is to say into internal energy. The work of the electric forces produces two source terms : the first one is the scalar

product of the electric field $\overrightarrow{E_k^0}$ and of the diffusion current $\overrightarrow{I_k^0} - \rho_k^0 Z_k^0 \overrightarrow{V_k^0}$, which is the electric current measured in the barycentric reference frame. It can be seen as Joule heating, that is as a conversion of potential energy into internal energy. The other part $\rho_k^0 Z_k^0 \overrightarrow{V_k^0} \cdot \overrightarrow{E_k^0}$ results in a motion of the electric charges subject to the electric field; potential energy is thus transformed into kinetic energy. Furthermore, the energy conservation law is consequently satisfied. Accordingly, there is no source term in the balance equation of the total energy.

We can examine in the same way the balance equations for one phase averaged over the R.E.V. That highlights the source terms

$$
\begin{array}{c|ccc}
 & E_c \longleftrightarrow E_p & U \longleftrightarrow E_p & E_c \longleftrightarrow U \\
\hline
E_{pk} & -\rho_k Z_k \overrightarrow{V_k} \cdot \overrightarrow{E_k} & -\overrightarrow{i_k} \cdot \overrightarrow{E_k} & \\
E_{ck} & +\rho_k Z_k \overrightarrow{V_k} \cdot \overrightarrow{E_k} & & -\underline{\sigma}_k : \underrightarrow{grad\overrightarrow{V_k}} \\
U_k & & +\overrightarrow{i_k} \cdot \overrightarrow{E_k} & +\underline{\sigma}_k : \underrightarrow{grad\overrightarrow{V_k}}
\end{array}
\tag{82}
$$

Viscous dissipation and Joule heating transform kinetic energy and potential energy into internal energy, respectively. And conversion of potential energy into kinetic energy is due once more to electric charges motion subject to the effect of the electric field. The other terms of the equations can be presented in the form

$$
\begin{array}{c|cc}
 & \text{flux} & \text{interfacial exchanges} \\
\hline
E_{pk} & & \\
E_{ck} & div\left(\underline{\sigma}_k \overrightarrow{V_k}\right) & +\overrightarrow{F_k} \cdot \overrightarrow{V_k} \\
U_k & -div\overrightarrow{Q_k} & -\left\langle \overrightarrow{Q_k^0} \cdot \overrightarrow{n_k} \chi_i \right\rangle \\
E_k & div\left(\underline{\sigma}_k \cdot \overrightarrow{V_k} - \overrightarrow{Q_k}\right) & +\overrightarrow{F_k} \cdot \overrightarrow{V_k} + P_k
\end{array}
\tag{83}
$$

where

$$
\begin{aligned}
\overrightarrow{F_k} \cdot \overrightarrow{V_k} &= \left\langle \left(\underline{\sigma}_k^0 \cdot \overrightarrow{n_k}\right) \cdot \overrightarrow{V_k^0} \chi_i \right\rangle \\
P_k &= \left\langle -\overrightarrow{Q_k^0} \cdot \overrightarrow{n_k} \chi_i \right\rangle
\end{aligned}
\tag{84}
$$

As before, the flux of internal energy is the heat transfer by conduction, and the flux of kinetic energy is the volume power of the contact forces within the phase. Additional terms arise from this analysis; they represent exchanges between the phases through the interfaces. $\overrightarrow{F_k} \cdot \overrightarrow{V_k}$ is thus the volume power of the interaction forces acting on the phase k and corresponds to a kinetic energy input. $-\left\langle \overrightarrow{Q_k^0} \cdot \overrightarrow{n_k} \chi_i \right\rangle$ results from the heat transfer through the interface and modifies the internal energy. The sum of these two terms modifies the total energy of the considered phase.

Concerning the whole E.A.P., we obtain the following decomposition

	flux
E_p	
E_c	$div \left[\sum\limits_{3,4} \left(\underline{\sigma}_k \cdot \overrightarrow{V_k} - E_{ck}\overrightarrow{V_k} \right) + E_c \overrightarrow{V} \right] + \frac{\partial}{\partial t} \left(E_c - \sum\limits_{3,4} E_{ck} \right)$
U	$div \left[\sum\limits_{3,4} E_{ck}\overrightarrow{V_k} - E_c \overrightarrow{V} - \overrightarrow{Q} \right] + \frac{\partial}{\partial t} \left(\sum\limits_{3,4} E_{ck} - E_c \right)$
E	$div \left(\sum\limits_{3,4} \underline{\sigma}_k \cdot \overrightarrow{V_k} - \overrightarrow{Q} \right)$

$$(85)$$

and

	$E_c \longleftrightarrow E_p$	$U \longleftrightarrow E_p$	$E_c \longleftrightarrow U$
E_p	$- \left(\sum\limits_{k=3,4} \left(\rho_k Z_k \overrightarrow{V_k} \right) + Z_i \overrightarrow{V_i} \right) \cdot \overrightarrow{E}$	$- \overrightarrow{i} \cdot \overrightarrow{E}$	
E_c	$+ \left(\sum\limits_{3,4} \rho_k Z_k \overrightarrow{V_k} + Z_i \overrightarrow{V_i} \right) \cdot \overrightarrow{E}$		$- \sum\limits_{3,4} \underline{\sigma}_k : \underline{grad}\overrightarrow{V_k}$
U		$+ \overrightarrow{i} \cdot \overrightarrow{E}$	$+ \sum\limits_{3,4} \left(\underline{\sigma}_k : \underline{grad}\overrightarrow{V_k} \right)$

$$(86)$$

The energy flux comes from the work of the contact forces in the different phases and from the heat transfer by conduction; the first one is a flux of kinetic energy, the second one is the flux of internal energy. The flux of potential energy is still zero. An additional flux term appears : the kinetic energy of the different phases measured in a barycentric reference frame; this kinetic energy is indeed a part of the internal energy of the global material. The source terms include viscous dissipation, which transforms kinetic energy into heat, and Joule heating, which transforms potential energy into internal energy. This last term is linked to the diffusion current created by the interfacial charges motion and by the cations motion in the solution reference frame. The global motion of the charges under the influence of the electric field turns potential energy on kinetic energy.

8 Conclusion

We have modelled an electroactive, ionic, water-saturated polymer placed in an electric field. The polymer is fully dissociated, releasing cations of small size. This system is depicted as the superposition of two continuous media : a deformable porous medium constituted by the polymer backbone embedded with anions, in which flows an ionic solution composed by water and released cations. We have deduced the microscale conservation laws of each phase : mass continuity equation, linear momentum conservation law, Maxwell's equations

and energy balance laws. Then we derived the physical quantities attached to the interfaces. An average over the R.E.V. of the material has provided one with macroscale conservation laws for each phase first and for the global E.A.P., next. Having the three constituents of the material (solid, solvent and cations) different velocities, we have used for this last step, the material derivative concept in order to obtain an Eulerian formulation of the conservation laws.

We have examined the balance equations of the different energies (kinetic, potential and internal ones), and we have put the emphasis on the phenomena responsible for the conversion of one kind of energy into another : viscous frictions, Joule effect and charge motion under the effect of the electric field. The first two results in dissipation. Moreover, the macroscale equations relative to each phase allow an evaluation of energy exchanges through the interfaces.

Using the linear thermodynamics of the irreversible processes we should now be able to determine the potential of dissipation and to derive the phenomenological equations governing this system. This will be the subject of a forthcoming work.

9 Appendix : interface modelling

In practice, contact area between phases 3 and 4 has a certain thickness; extensive physical quantities like mass density, linear momentum and energy continuously vary from one bulk phase to the other one. This complicated reality can be modelled by two uniform bulk phases separated by a discontinuity surface Σ whose localization is arbitrary. Let Ω be a cylinder crossing Σ, whose bases are parallel to Σ. We denote by Ω_3 and Ω_4 the parts of Σ respectively included in phases 3 and 4.

The continuous quantities relative to the contact zone are identified by a superscript ^{0} and no subscript. A microscale quantity per surface unit g_i^0 related to the interface is defined by

$$g_i^0 = \lim_{\Sigma \longrightarrow 0} \frac{1}{\Sigma} \left\{ \int_\Omega g^0 dv - \int_{\Omega_3} g_3^0 dv - \int_{\Omega_4} g_4^0 dv \right\} \tag{87}$$

where Ω_3 and Ω_4 are small enough so that g_3^0 and g_4^0 are constant. Its average over the R.E.V. is the volume quantity g_i defined by

$$g_i = \left\langle g_i^0 \chi_i \right\rangle \tag{88}$$

The balance equation of the interfacial quantity g_i^0 is written as (Ishii, [20])

$$\frac{\partial g_i^0}{\partial t} + div_s \left(g_i^0 \overrightarrow{V_i^0} \right) = \sum_{3,4} \left[g_k^0 \left(\overrightarrow{V_k} - \overrightarrow{V_i^0} \right) \cdot \overrightarrow{n_k} + \overrightarrow{J_k^0} \cdot \overrightarrow{n_k} \right] - div_s \overrightarrow{J_i^0} + \phi_i^0$$

where div_s denotes the surface divergence operator. $\overrightarrow{J_i^0}$ is the surface flux of g_i^0, $\overrightarrow{J_k^0}$ the flux of g_k^0 and ϕ_i^0 the surface source term.

We arbitrarily fix the interface position in such a way that it has no mass density

$$\rho_i^0 = \lim_{\Sigma \longrightarrow 0} \frac{1}{\Sigma} \left\{ \int_\Omega \rho^0 dv - \int_{\Omega_3} \rho_3^0 dv - \int_{\Omega_4} \rho_4^0 dv \right\} = 0 \tag{89}$$

From (6), we deduce that the linear momentum and the kinetic energy per surface unit of the interface, respectively denoted $\overrightarrow{P_i^0}$ and E_{ci}^0, are zero

$$\overrightarrow{P_i^0} = \overrightarrow{0} \qquad\qquad E_{ci}^0 = 0 \tag{90}$$

In the same way, we define the charge per unit surface Z_i^0, the surface current vector $\overrightarrow{I_i^0}$, the surface diffusion current $\overrightarrow{i_i^0}$, the surface potential energy E_{pi}^0, the surface internal energy U_i^0 and the surface total energy E_i^0.

The balance equations of these quantities write

$$\frac{\partial Z_i^0}{\partial t} + div_s \left(Z_i^0 \overrightarrow{V_i^0} \right) = \overrightarrow{i_3^0} \cdot \overrightarrow{n_3} + \overrightarrow{i_4^0} \cdot \overrightarrow{n_4} - div_s \overrightarrow{i_i^0} \tag{91}$$

$$\frac{\partial \overrightarrow{P_i^0}}{\partial t} + \overrightarrow{div_s} \left(\overrightarrow{P_i^0} \otimes \overrightarrow{V_i^0} \right) = -\underline{\sigma}_3^0 \cdot \overrightarrow{n_3} - \underline{\sigma}_4^0 \cdot \overrightarrow{n_4} + Z_i^0 \overrightarrow{E_i^0} \tag{92}$$

$$\frac{\partial E_{pi}^0}{\partial t} + div_s \left(E_{pi}^0 \overrightarrow{V_i^0} \right) = -\overrightarrow{I_i^0} \cdot \overrightarrow{E_i^0} \tag{93}$$

$$\frac{\partial E_i^0}{\partial t} + div_s \left(E_i^0 \overrightarrow{V_i^0} \right) = -\left(\underline{\sigma}_3^0 \cdot \overrightarrow{n_3} \right) \cdot \overrightarrow{V_3^0} - \left(\underline{\sigma}_4^0 \cdot \overrightarrow{n_4} \right) \cdot \overrightarrow{V_4^0} + \overrightarrow{Q_3^0} \cdot \overrightarrow{n_3} + \overrightarrow{Q_4^0} \cdot \overrightarrow{n_4} \tag{94}$$

$$\frac{\partial U_i^0}{\partial t} + div_s \left(U_i^0 \overrightarrow{V_i^0} \right) = \overrightarrow{Q_3^0} \cdot \overrightarrow{n_3} + \overrightarrow{Q_4^0} \cdot \overrightarrow{n_4} + \overrightarrow{i_i^0} \cdot \overrightarrow{E_i^0} \tag{95}$$

Averaging over the R.E.V., this leads to the boundary conditions below

$$\frac{\partial Z_i}{\partial t} + div \overrightarrow{I_i} = \left\langle \overrightarrow{i_3^0} \cdot \overrightarrow{n_3} \chi_i \right\rangle + \left\langle \overrightarrow{i_4^0} \cdot \overrightarrow{n_4} \chi_i \right\rangle \tag{96}$$

$$\overrightarrow{F_3} + \overrightarrow{F_4} = Z_i \overrightarrow{E_i} \tag{97}$$

$$\frac{\partial E_{pi}}{\partial t} + div \left(E_{pi} \overrightarrow{V_i} \right) = -\overrightarrow{I_i} \cdot \overrightarrow{E_i} \tag{98}$$

$$\frac{\partial E_i}{\partial t} + div_s \left(E_i \overrightarrow{V_i} \right) = -P_3 - P_4 - \overrightarrow{F_3} \cdot \overrightarrow{V_3} - \overrightarrow{F_4} \cdot \overrightarrow{V_4} \tag{99}$$

$$\frac{\partial U_i}{\partial t} + div \left(U_i \overrightarrow{V_i} \right) = \left\langle \overrightarrow{Q_3^0} \cdot \overrightarrow{n_3} \chi_i + \overrightarrow{Q_4^0} \cdot \overrightarrow{n_4} \chi_i \right\rangle + \overrightarrow{i_i} \cdot \overrightarrow{E_i} \tag{100}$$

Moreover, we have

$$\overrightarrow{I_i} = Z_i \overrightarrow{V_i} + \overrightarrow{i_i}$$

10 Notations

$k = 1, 2, 3, 4, i$ subscripts respectively represent cations, solvent, solid, solution (water and cations) and interface; quantities without subscript refer to the whole material. Superscript ^{0} denotes a local quantity; the lack of superscript indicates average quantity at the macroscopic scale. Microscale volume quantities are relative to the volume of the phase, average quantities to the volume of the whole material.

C : cations molar concentration (relative to the liquid phase);

$\overrightarrow{D}$ $(\overrightarrow{D_k}, \overrightarrow{D_k^0})$: electric displacement field;

E (E_k, E_k^0) : total energy density (internal, kinetic and potential);

$\overrightarrow{E}$ $(\overrightarrow{E_k}, \overrightarrow{E_k^0})$: electric field;

E_c $(E_{c\Sigma}, E_{ck}, E_{ck}^0)$: kinetic energy density;

E_p (E_{pk}, E_{pk}^0) : potential energy density;

$F = 96487 \ C \ mol^{-1}$: Faraday's constant ;

$\overrightarrow{F_k}$: resultant of the mechanical stresses exerted on the phase k by the other phase;

$\overrightarrow{I}$ $(\overrightarrow{I_k}, \overrightarrow{I_k^0})$: current density vector;

$\overrightarrow{i}$ $(\overrightarrow{i_k}, \overrightarrow{i_k^0})$: diffusion current;

M_k : molar mass of component k;

$\overrightarrow{n_k}$: outward-pointing unit normal of phase k;

P_k : heat flux through interfaces;

$\overrightarrow{P_i^0}$: local surface linear momentum of interface;

$\overrightarrow{Q}$ $(\overrightarrow{Q_k}, \overrightarrow{Q_k^0})$: heat flux;

U (U_Σ, U_k, U_k^0) : internal energy density;

$\overrightarrow{V}$ $(\overrightarrow{V_k}, \overrightarrow{V_k^0})$: velocity;

z_k : number of elementary charges of a ion k;

Z (Z_k, Z_k^0) : total electric charge per unit of mass;

Z_i (Z_i^0) : electric charge density per unit surface;

ε $(\varepsilon_k, \varepsilon_k^0)$: permittivity;

ρ (ρ_k, ρ_k^0) : mass density;

$\underline{\sigma}$ $(\underline{\sigma}_k, \underline{\sigma}_k^0)$: stress tensor;

ϕ_k : volume fraction of phase k;

χ_k : function of presence of phase k ;

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