Research Summary:
The Effect of Microstructure on the Macroscopic Response of Electroactive Systems

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Abstract—A framework to model the effect of the microstructural features and crystallographic anisotropy on the macroscopic response of electroactive ceramics is described. The model accounts for mechanical, electric and concentration fields, as well as couplings such as piezoelectricity and electromigration. The setup starts from single crystal properties and incorporates them into a numerical setup by applying on the finite element method. This was implemented by modifying the Object Oriented Finite Element Analysis for Materials Science software (OOF). The model is validated against analytic solutions.

This framework is applied to describe a) the effect of crystallographic texture and grain microstructure in ceramic ferroelectrics and b) the transport processes of charged species for rechargeable Li-ion batteries.

I. INTRODUCTION

Progress for high-performance electromechanical actuators and sensors depends, in part, on the development of novel materials, design of device architecture, amplification mechanisms, and processing to create optimal microstructures [1].

In ferroelectric materials, the effect of microstructure on the local state of stress and polarization state are not simple to model because the fields are coupled, and the coupling is not necessarily spatially uniform. Furthermore, reliable models to analyze the macroscopic behavior that derives from the microstructure depend upon the proper incorporation of the physical properties at a microstructural level.

Nowadays there is an increasing interest in improving the performance of rechargeable Li-ion batteries. In recent years new materials and device architectures have been explored in an attempt to increase its power and energy density.

A rechargeable battery is formed of three parts: Anode, cathode and separator. The particular internal features of each part depend on the design, and characteristics of the materials involved. During the charging and discharging (cycling) of a battery, the internal geometrical features that describe the cathode and anode (and even any possible relevant features that can be found on the separator) influence the local transport of Li-ions and electrons. These spatial inhomogeneities induce localized fluxes and gradients of concentration and voltage that ultimately control the macroscopic response of the system. In this context, study and understanding of the interrelation between the microstructure and properties during cycling of a battery becomes very important. In an attempt to understand and propose some criteria to improve the power and energy density of these systems, in the rest of this paper a formulation based on irreversible thermodynamics is proposed. This formulation is implemented by applying the Finite Element method in order to account for the physics and effect of microstructure of rechargeable batteries. It is described generality regarding boundary conditions.

II. MODELLING OF TEXTURED FERROELECTRIC CERAMICS

A. Theoretical Framework

A thermodynamically reversible change in the state of polarization and stress of a piezoelectric solid can be described in terms of two first order Taylor series expansions around the equilibrium state. So, for an initially stress free and polarization free solid

\[ D_i = \varepsilon_{ij}^T E_j + d_{im} C_{lmjk} \varepsilon_{jk} \]  

\[ \sigma_{ij} = C_{ijkl}^E (\varepsilon_{ij}^T - d_{mkl} E_m) \]  

\( \varepsilon_{ij}^T \) is the \( ij \)-th component of total deformation tensor (i.e., the sum of two contributions, one due to elastic deformation in the absence of an electric field and the other due to a stress-free application of an electric field), and \( E_k \) is the \( k \)-th component of the electric field. \( d_{mkl} \) is the piezoelectric tensor, \( C_{ijkl}^E \) is the stiffness tensor at constant electric field, and \( \varepsilon_{ij}^T \) is the dielectric permittivity at constant stress. In Equation 2, the first entry corresponds to Hooke’s law. The second term of this equation can be identified as the contribution to the total deformation due to the converse piezoelectric effect. Equation 1 describes the different contributions to polarization in the solid. In some materials and crystal structures, higher order effects may become important under particular boundary conditions. For this case, the properties can be regarded as a function of the intensive quantities. We will follow the approach developed by [2]. In the most general case, by expanding the physical properties in a Taylor series expansion to first
order for the intensive quantities, so that

\[\epsilon'_{ij} = \epsilon'_{ij,o} + \frac{\partial \epsilon'_{ij}}{\partial \sigma_{kl}} \sigma_{kl} + \frac{\partial \epsilon'_{ij}}{\partial E_k} E_k\]  

(3)

\[d_{ijk} = d_{ijk}^o + \frac{\partial d_{ijk}}{\partial \sigma_{lm}} \sigma_{lm} + \frac{\partial d_{ijk}}{\partial E_l} E_l\]  

(4)

For which for non-electrooptic solids

\[d_{ijk} = d_{ijk,o} + Q_{ijmn} \kappa_{mn}^s \kappa_{mn}^e E_l\]  

(5)

as the effective piezoelectric tensor, and

\[\epsilon'_{ij} = (\epsilon'_{ij,o} - d_{jm}{^C} \delta_{mn} d_{ikl} + C_{ijkl} Q_{klpq} \kappa_{pq}^s \kappa_{pq}^e \varepsilon_{rs})\]  

(6)

as the total permittivity tensor. The equilibrium equations can be found by the application of calculus of variations, finding

\[\nabla \cdot \vec{\sigma} = 0\]
\[\nabla \cdot \vec{D} = 0\]  

(7)

This set of equations describes the continuity of forces across geometrical interfaces, together with the continuity of polarization in the absence of gravity and net electrostatic charges. The second equation is one of the well-known Maxwell equations for electrostatics.

B. Finite Element Approximation

The finite element approximation is introduced by discretizing \( \Omega \) into a set of connected subregions (elements). Within each element \( m \), the fields are described by linear combinations of functions \( N^m_j \) (trial functions), for which for triangular linear elements

\[N^m_j(x,y) = \frac{a^m_j + b^m_j x + c^m_j y}{2\Delta}\]  

(8)

Here \( a^m_j, b^m_j, c^m_j \) are constants and \( \Delta \) is the area of the triangular element.

For the above setup, we want to consider the case in which a generalized ferroelectric ceramic is spatially coupled within a two dimensional plane, but free to deform out of the plane. This situation corresponds to a solid in plane stress, whose properties do not change significantly out of the plane, such as a ferroelectric film. We will follow a procedure similar to the one used by [3]. The final set of equations are given by [4], [5], [6]: a set of coupled linear equations, that in their final form depend on the underlying mesh that derived from the particular microstructure being studied. The final system has the form

\[K\vec{V} = \vec{f}\]  

(9)

where \( \vec{V} \) is a vector that has one component for each unknown variable, being either displacement or nodal voltage. Each of these unknowns is called a degree of freedom. \( K \) is an \( M \times M \) matrix and is known as the global stiffness matrix. \( M \) is the total number of degrees of freedom. \( \vec{f} \) is a vector that assembles the contributions from body forces, surface forces, electrostatic surface charges and user-specified boundary voltages and displacements, for each of the corresponding nodal variables.

Equation 9 can be solved by applying standard numerical methods. In the current approach [3], [7], [8], [9] applies the Conjugate Gradient method [10], [11]. In the application of this method, an approximation to the solution of Equation 9 is reached by iterating over a succession of steps until a user-specified limit (error or tolerance for convergence) is reached or a maximum number of iterations is performed.

C. Higher Order Effects

Let us assume that we initially know the solution to Equations 1 and 2. For such case, it can be found a modified global system that has the following form:

\[K(\vec{V})\vec{V} = \vec{f}(\vec{V})\]  

(10)

Equation 10 constitutes a set of coupled non-linear algebraic equations that can be solved by applying the Newton-Raphson method [12].

D. Model Validation

In order to verify our model, a simple set of simulations was performed. A hypothetical 1 x 1 m square sample composed entirely of a single crystal piezoelectric with isotropic dielectric properties, very compliant stiffness tensor, and piezoelectric coefficients equal to the one from Barium Titanate [13], [14] was simulated with a 100 V difference applied between two of its (non-adjacent) sides. Mechanically, all the edges were free to deform in space. The remaining sides were left free from any specified boundary conditions, i.e., under plane stress conditions.

The crystal was initially oriented such that its c-axis was parallel to the x-axis of the laboratory reference system. The c-axis was then rotated about the x-axis so that the c-axis was misoriented by an angle \( \theta \). The deformation tensor and electric field was calculated by OOF in response to this voltage difference. The calculation was repeated for different angles \( \theta \) and is reported in Figure 1. The agreement between the exact solution and the OOF prediction is excellent.

The expected a uniform electric field along the x-direction. The expected deformation in the direction of the field is given by

\[\varepsilon_{11} = (\varepsilon_{11}^o - \varepsilon_o) Q_{11} E^2\]  

(11)

A comparison between the predicted and observed response can be seen in Figure 2.

E. Selected Results

Simulations are carried out to study the effect of crystallographic texture and grain size on the macroscopic properties of polycrystalline BaTiO3 and PZN-PT. It is demonstrated that, for materials belonging to point group 4mm,
if the single crystal piezoelectric constant $d_{15}$ is greater than $d_{31}$ and $d_{33}$, then an apparent enhancement in the macroscopic piezoelectric response of $d_{31}$ and $d_{33}$, will be observed for the polycrystalline samples and an optimal response occurs for samples that are not perfectly textured, but have particular randomness in crystallographic grain orientations. If $d_{15}$ is smaller than $d_{31}$ and $d_{33}$, an apparent enhancement in $d_{15}$ will be observed, which may be suitable for actuators/sensors that are used in shear mode. The optimal texture parameters were found to be $r = 0.7$ (or 2.9 MRD), with an equivalent optimal cone angle of 46.78 degrees.

III. MODELLING OF MICROSTRUCTURAL EFFECTS IN LI-ION BATTERIES

A. Theoretical Framework

Let us define the mass flux of lithium ions as $N_{Li}^{*}$, the total mass flux of charge as $\vec{J}_{q}$.

$$
\begin{align*}
N_{Li}^{*} &= -D_{Li} \nabla c_{Li} - M_{Li} c_{Li} \nabla \phi \\
\vec{J}_{q} &= -M_{Li} c_{Li} \nabla c_{Li} + M_{ec} c_{e} \nabla c_{e} - (\sigma_{e} + M_{Li}^{*} c_{Li}) \nabla \phi \tag{12}
\end{align*}
$$

$M_{Li}^{*}$ the electric ion mobility for ionized lithium, so that the electric conductivity corresponding to Li is given by $\sigma_{Li} = M_{Li}^{*} c_{Li}$. $c_{Li}$ is the local concentration of lithium, $c_{e}$ is the concentration of electrons and $D_{i}$ the intrinsic diffusivity.

By applying concepts of irreversible thermodynamics [15],

$$
\begin{align*}
\frac{\partial \sigma_{e}}{\partial t} &= \nabla \cdot (D_{e} \nabla c_{e}) + \nabla \cdot (M_{Li} c_{Li} \nabla \phi) \\
\frac{\partial M_{Li} c_{Li}}{\partial t} &= \nabla \cdot (D_{Li} c_{Li}) - \nabla \cdot (M_{Li} c_{Li} \nabla \phi) \\
0 &= \nabla \cdot ((\sigma_{Li} + \sigma_{e}) \nabla \phi) + \nabla \cdot (M_{Li} c_{Li} \nabla c_{Li}) - \nabla \cdot (M_{e} c_{e} \nabla c_{e}) \tag{13}
\end{align*}
$$

B. Particle-Electrolyte Interfacial Kinetics

A particle in the cathode or anode is embedded in an electrolytic medium and exchanges lithium with its surroundings. This exchange process is controlled by the involved driving forces, which in this case are the gradients of voltage (electric field), and concentration of lithium ions and electrons. Qualitatively, at the particle-electrolyte interface for each lithium ion it is needed an electron to intercalate inside the particle. If occurring at equilibrium, it would be governed by the reaction

$$
\text{Li}^{+} + e^{-} \rightleftharpoons \text{Li} \tag{14}
$$

However, out of equilibrium, the rate of transfer of lithium ions is lower than the corresponding one of electrons, inducing a local gradient of electric potential, that controls the transference of both ionized species. At this interface the

$$
\vec{J}_{q}^{\text{int}} = \vec{J}_{q} \left( e^{\frac{\alpha_{Li} E}{kT}} - e^{\frac{\alpha_{e} E}{kT}} \right) \tag{15}
$$
where the first term correspond to the forward rate of the anodic process, which is modulated by an empirical coefficient $\alpha_\alpha$. Likewise, $\alpha_c$ is the empirical parameter associated with the rate of the backward cathodic reaction. $F$ is the well-known Faraday constant, $R$ is the gas constant, $T$ is the absolute temperature, and $\eta$ is the so-called local overpotential. Equation 15 is known as the Butler-Volmer equation. Physically, a particle-electrolyte interface that satisfies this equation, would not allow exchange of lithium ions and electrons unless an overpotential $\eta \neq 0$ is induced at that particular point of the interface (i.e., a required energetic penalty must be paid in order for transference of the involved species). At equilibrium, the forward and backwards rate of reaction is effectively balanced, leading to have a total charge current of zero.

The surface overpotential $\eta$ is described by the proposed relation

$$\eta = (\Delta \phi - \phi_o)$$

(16)

$\phi_o$ is the so-called contact potential. $z$ is the valence of the ionic species considered. $\Delta \phi$ is the local voltage drop at the particle-electrolyte interface. Equation 15 describes the exchange of flux of charge between the particle and its surroundings, controlled by the electrochemical potential. In this particular case, the transfer of charged species is solely controlled by the overpotential, where $\phi_o$ may in the most arbitrary case depend on composition [16, 17].

### C. Finite Element Approximation

By using the same finite element approximation as described above, the local fields and the spatial correlations between the different microstructural features were described, resulting on the set of equations for the $i$-element

$$K_i \ddot{u}_i + C_i \dot{u}_i = f_i$$

(17)

so that $K_i$ is the so-called stiffness matrix, $C$ is the conductivity matrix, with $\ddot{u}_i$ the vector of nodal concentrations and voltages. $\dot{u}_i$ is the time derivative of the nodal
concentrations and voltages. Finally, $f_{\bar{u}}$, a vector comprised by the contributions from fixed mass and ion fluxes at the boundaries.

The matrices associated with Equation 17 can be calculated for every element, leading to a global set of coupled linear equations. The final form of these depends on the underlying mesh that derived from the particular microstructure that we are studying. The final system has the form

$$K\bar{u} + C\dot{\bar{u}} = \bar{f}$$

(18)

where $\bar{u}$ is a vector that has one component for each unknown variable, being either concentration or nodal voltage.

D. Model Validation

This model was validated by comparing it against analytic solutions. In Figure 6 can be seen the diffusion of an uncharged species across 100 $\mu$m after one ms. The imposed boundary conditions are the following. On the left edge concentration was fixed to be one. On the right edge the concentration was fixed to zero. Diffusivity was arbitrarily fixed to be $1 \times 10^{-10}$. It was also verified that after 5 minutes, the system reached steady state.

E. Selected Results

In Figure 7 can be observed the normalized concentration distribution of lithium ions inside a 200 $\mu$m cathode. Preliminary results suggest that the spatial distribution of LiMO$_2$ particles, particle size, as well as boundary conditions influence power an energy density of the system. Selected caption illustrates that percolated particles shield the ones on the back part (right) of the cathode, influencing and thus decreasing the power density of the overall device.

REFERENCES

Figure 7 On top, typical microstructure of a cathode of a rechargeable battery. Middle figure describes concentration distribution of short-circuited battery after 30 seconds. Bottom caption shows distribution of lithium ions after 5 minutes.