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Nano-Mechanics foundations and experimental methodologies for multiphysics prognosis of functional behaviour in heterogeneous functional materials (HeteroFoaM)

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Abstract

The present paper will discuss the nano-mechanics foundations and experimental methodologies that provide a foundation for the prognosis of the functional behavior of nano-structured heterogeneous materials for energy systems. The principle objective of this work at the fundamental level is the creation of conceptual foundations for prognosis of heterogeneous functional materials. Our approach is to focus on the mechanics associated with the nano-structural configurations and interfaces (function and geometry) of the active phases. The paper will discuss conceptual foundations, experimental methods, and computational and analysis methods that associate global functional response of interest to energy conversion and storage with the multiphysics of nano-structured heterogeneous materials. New experimental room-temperature, non-invasive interrogation methods for establishing internal integrity and for following material state changes in solid oxide fuel cells as a function of operation history will also be introduced and discussed as an example of the application of these concepts.

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1. Background

In many ways, the future of our society will be determined by the materials we are able to design and make. For heterogeneous materials, this requires a fundamental understanding and predictive capability to make material systems from micro- or nano-sized bits of different materials, that have controlled shapes, properties, and interfaces that enable them to interact and act together to function as a system. Such

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functional heterogeneous materials interact with their environments to catalyze, conduct, emit, absorb, convert or otherwise alter them in various ways, and are used in membranes, electrodes and forms that make it possible to create critical medical, energy, and material processing devices. Nano-structured heterogeneous functional materials (HeteroFoaMs) are literally disruptive material concepts, in the sense that they have quickly replaced homogeneous materials in a host of energy-centric devices that make electrochemistry, fuel synthesis, chemical refinement, hydrogen storage, heat storage, and other essential processes possible. The challenge for science and engineering is to replace largely Edisonian current methods of design and synthesis of such material systems by fundamental understanding and robust models. Specifically we must establish the control science that enables simulation-based design and creation of the nanostructural configurations and interfaces (physics, chemistry, and geometry) of the active phases.

An example of a HeteroFoaM material is shown in Fig. 1. The description of the balance of mass, momentum, energy and charge, associated boundary conditions and constitutive equations that describe how these systems work is an active frontier of science. The authors have demonstrated some of the details of that enterprise [1−6] and many other representations have appeared in [7]. For present purposes we ask the question, how can we use the full rigor of the physics (and specifically the mechanics) of this problem to address the question of prognosis of functional performance of such a material system, as a function of how it is made and what collective material state it has at a given operational juncture?
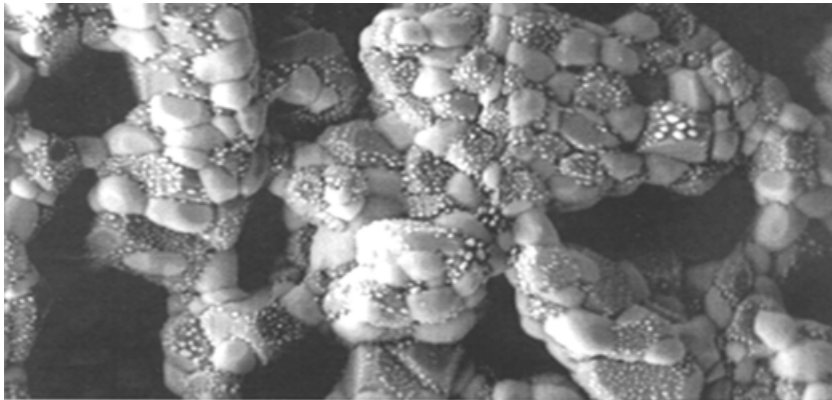

Fig. 1. Example of HeteroFoaM material (anode of a solid oxide fuel cell) showing several functional phases including void phases that transport fuel to electrochemical surfaces and interfaces

The concept of prognosis is typically discussed in terms of mechanical characteristics such as structural integrity, durability, damage tolerance, fracture toughness, etc. These familiar concepts are usually addressed by considering balance equations, crack growth relationships, and constitutive equations with constant material properties, and constant or cyclically applied load conditions. Loading histories are represented by changing stress (or strain) states, only. But for many situations, especially associated with high performance engineering structures, the local state of the material may also change during service, so that the properties used in those equations are functions of time and history of applied conditions. In addition, for many energy systems, a broader definition is required. For example, in fuel cells, properties such as conductivity and electrochemical character are altered by material degradation, so that "property fields" replace the global constants in the associated multiphysics balance equations, and time and history enter into the governing equations. Moreover, the local mechanical integrity of the materials in a fuel cell also controls the functional performance of the electrochemical device. The present paper reports the first direct interpretation of that relationship, based on the idea that material compliance

with applied fields is a direct measure of the structural integrity of the material system and of its ability to do functional "work", which has exact mechanical as well as electrochemical or other multiphysics interpretations.

In the present paper we introduce this concept of generalized material compliance as a foundation for the mechanics of prognosis of HeteroFoaM materials. We will show experimental results that lead us to this concept and construct a rigorous model for the example of applied mechanical and electrical fields in a variety of heterogeneous material systems. Then we will illustrate the power of the model and concept by focusing on a very specific example of the application of the concepts to the prediction of progressive changes in generalized compliance during the degradation of a composite material under mechanical loading.

2. The concept of heterogeneous functional material design

Design of heterogeneous functional materials such as those shown in Fig. 1 begins with the requirements that drive the selection of the constituents. For fuel cells, for example, electrodes must have electronic and ionic conduction capability, and must facilitate electrochemistry by catalytic properties. Constituent materials for batteries must also have electrochemical properties, with additional transport characteristics. Separation membranes must selectively transport mass, usually in ionic form, and must often also be a mixed ionic and electronic conductor. These and other requirements generally drive the specification of the intrinsic properties and characteristics that define the constituents of the materials in the heterogeneous mixture.

Heterogeneous functional materials, however, are material systems; their constituents act together and interact to create functional behavior such as the conversion of chemical energy from fuel to electrical energy, separation of oxides from mineral ores or nuclear waste stock, or storing electrical charge in a capacitor. This functional capability is greatly dependent on the extrinsic character of the material system. In some cases, these extrinsic features are easy to identify. The size, shape, surface and interface characteristics, and morphological arrangement of the constituents play critical roles in the functionality. If active void phases are present, these features include those constituent "phases" as well. Other extrinsic characteristics are not so easily identified. The defect structure in materials is a good example of the extrinsic properties that can play even a dominant role in the character of the heterogeneous material. And finally, the scale of the heterogeneity is often important. Often the ionic conductivity of materials which is so important to many such systems is created by defect chemistry at the atomic and nano-levels, while micro-crack formation which may dominate mechanical properties may occur at dimensions that are three or four orders of magnitude greater in dimensions.

It is the premise of this paper that any proper design of heterogeneous functional materials, or HeteroFoaM as a genus, must address the extrinsic as well as the intrinsic characteristics of the material system, across multiply length scales. Moreover, we will show below that a multiphysics approach to that design benefits from general conceptual principles that can be applied across several essential aspects of the response of those systems, e.g., the mechanical and electrical character.

3. Mechanical and electrical fields in heterogeneous solids

For our discussion, we consider three classes of heterogeneity, idealized in Fig. 2. Figure 2a is a single phase material. That phase may be a homogenized version of a heterogeneous system, but in general, it is regarded and discussed as a single material. Figure 2b is a two phase material, in which the shape, size, and orientation of the second phase can be designed at our discretion. Figure 2c represents a matrix of one phase reinforced by a continuous fiber phase. The fibers have the usual delineations of volume fraction,

fiber diameter, fiber orientation, constituent properties and interfaces. For our present discussion, we will not admit a third phase at the interface between our two example phases, but that and other extensions of the reasoning are easily added to the discussion.
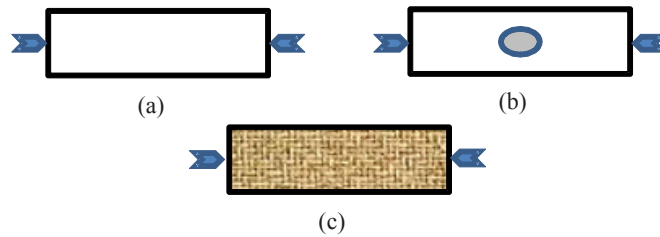

Fig. 2. Classes of heterogeneity considered: (a) Uniform; (b) Two phase; (c) Continuous fiber reinforced matrix

We consider a vector field applied to our example elements, suggested by the arrows on either end of the domains in Fig. 2. For our discussion of design and ultimately prognosis, we will consider only two types of applied fields, a uniaxial mechanical stress field and a vector electromagnetic field. For the uniform material case, we expect differential displacement of material points in response to the mechanical stress to create a uniform strain response throughout the element, in the usual spirit of mechanics of materials. If that response is conservative, we call it "elastic," and typically discuss a reversible proportionality between the applied field and the material response. If it is not conservative, we speak of "inelastic" behavior and expect to find some change in material state that results from the deformation. Simple evidence for that change of state may often be found in the change in the constitutive relationship between the applied (stress) field and the observed material (strain) response. For the case of an applied electric field, we will exclude the effects of free charge as simple conduction of electrical current is not of interest to us in the present discussion. For bound charge or stored charge, a typical assumption is that the charge displacement is proportional to the applied field, with the following notations commonly used as

$$D = \varepsilon_0 \varepsilon E, \qquad \varepsilon = \varepsilon' + \frac{\sigma}{i\omega\varepsilon_0}, \qquad (1)$$

where D is the charge displacement caused by the applied field E, ε_0 is the permittivity of vacuum, ε is the relative permittivity of our heterogeneous material with real part ε', ω is the frequency of harmonic changes in the applied field, and σ is the real conductivity of the material [1−6].

For our uniform material case, Fig. 2a, the applied field and the material response are linear throughout the element under consideration. The "compliance" of the material with the field is determined by the elastic modulus in the mechanical case, and by the compliance with the electric field, quite literally the permittivity, in the case of an applied electric field.

When a second phase enters the problem, as in Fig. 2b, the situation is more complex, but consistent with our expectations for both a mechanical and electrical situation. The mechanical situation is familiar to us. Second phases (e.g., a center hole in a plate specimen) introduce a local disturbance of the stress field to create a "concentration" of the field at the local level. And an important feature of that local concentration is the local energy stored by the concentration of the field. If the second phase is a void or crack, then the local stored energy may be great enough to induce local rupture and growth of the size of the local feature, even if there is no work being done on the specimen at the global level, i.e., the global boundaries are fixed [7].

There is comparable behavior for an applied electric field, although it is more difficult to quantify the nature of the local charge storage. Liu et al. have provided some recent clarity to this question [1−6]. Liu considers, for example, the local stored charge (called capacitance in that case) for inclusions of various shapes and sizes, as shown in Fig. 3 (left).

The boundary conditions for the representative volume elements shown in the left of Fig. 3 are symmetric across the edges of the domains, so that the model (in closed form) represents an array of included phase regions with a volume fraction that varies with the size of the particle in the domain. When volume fractions are large, the local field concentrations around the second phase particles interact to form a non-dilute solution. The analysis not only solves for the field throughout the region, but also solves for the internal surface charge at all locations on the two-phase interface that results from the discontinuous jump in properties across those interfaces. We have validated that analysis by making actual measurements not only of potential variations across the interfaces, but also we have made what may be the first direct measurements of surface charge as a function of position at those phase interfaces [6]. The total integrated charge storage is also determined from the analysis by applying an alternating current to the domains and calculating the real and imaginary parts of the permittivity as a function of frequency, to determine the quantities shown in Eq. (1).
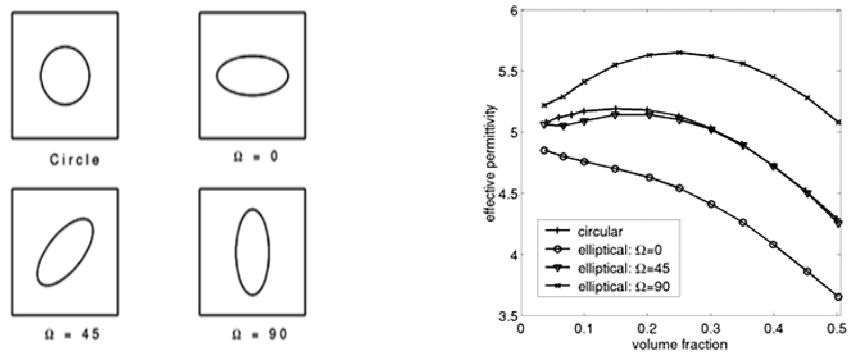

Fig. 3. Configurations analyzed (left) and stored charge in terms of "effective permittivity" (right)
for a two phase heterogeneous material

On the right of Fig. 3 a sample of those results is shown for circular and elliptical second phase regions as a function of volume fraction, and orientation of the elliptical axis of the included phase with the vector direction of the applied electric field. For that calculation, the matrix material had negligible conductivity but significant permittivity, while the inclusion had small but finite conductivity and small permittivity [6]. The reasons for choosing those relative conditions will be explained in the next section. The results shown in Fig. 3 are quite surprising. The effective permittivity (and therefore the stored charge – and the capacitance as an ability to do work) is not a monotonic function of the amount of the second phase. Moreover, the permittivity is highly dependent on the extrinsic character of the elliptical inclusions, not only their size and shape but also their orientation relative to the field. This is highly reminiscent of what we know to be true for the mechanical analogue to this situation (where the size, shape and orientation of a slit in a specimen has a profound effect on the nature of the local stress concentrations), but quite distinct in many of the nonlinear effects, especially in the increase followed by a decrease in the permittivity predicted for some of the conditions modeled in Fig. 3. The physical foundation for this surprising behavior is the tradeoff between the contributions of two distinct physical properties of the constituents that determine the total electrical permittivity, as shown in Eq. (1). Both the dielectric

permittivity and (for a heterogeneous material) the conductivity of the phases contribute to this result. So if this prediction has physical reality, we see that there is additional information that can be determined from the dielectric response for the case of an electric field in such materials, compared to the compliance with the mechanical applied stress.

4. Non-conservative changes in material state

If there is some interaction of the material domain with the incident fields, then if sufficient intensity of the field is applied, there is the potential for the field to induce changes in the physical state of the material. For an electric field, one can imagine the effect of insulation breakdown, a bolt of lightning, etc. We have data for this type of change, but that subject is, in general, beyond our reach in the present paper. However, we can consider changes in physical state caused by the application of mechanical fields. For that purpose, we consider glass fiber reinforced epoxy materials, of the type suggested in Fig. 1c, loaded into the inelastic range with a unidirectional stress field that is at some angle to the principle reinforcement directions of the material, an "off-axis" test in the language of that field. Many such data are available [8–10]. An example response is shown in Fig. 4.
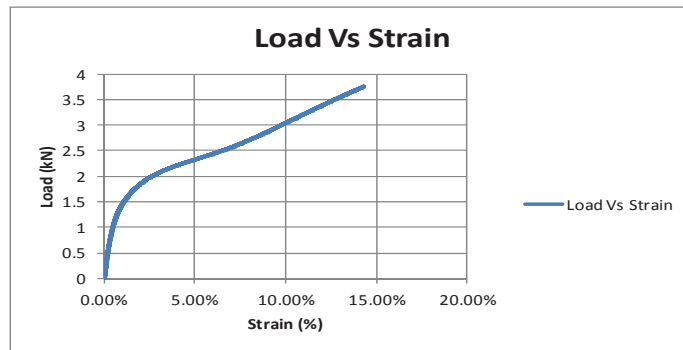

Fig. 4. Typical load strain behavior for off-axis loading of a woven fiber reinforced composite material

The authors have developed a fully nonlinear deformation plasticity constitutive law (in the form of Master curves) for such response that recovers the full effects of anisotropy and nonlinear response in previous publications [9, 10]. However, for present purposes, we wish to construct an approximate representation of the microcracking associated with the response in Fig. 4 as a simple foundation for discussing that process as the progressive introduction and accumulation (increasing volume fraction) of a "second phase" of cracked material in the specimen as loading and strain continues beyond the elastic range. One simplified concept that can be used to interpret material behavior is to require that the elastic stiffness of some of the constituents in the specimen be progressively reduced with degradation so that a linear (classical laminate) analysis follows the curve shown in Fig. 4. In fact, this "discounting method" is widely used for such generalized interpretations [11]. If one takes that approach, and plots the required values of the matrix-constituent elastic Young's modulus and shear modulus as a function of strain for the data shown in Fig. 4, the behavior shown in Fig. 5 results.

We learn from this exercise that there is a high rate of microcracking (and therefore a rapid increase in the volume fraction of our "crack phase") in the early part of the inelastic deformation, followed by a long period of substantial reductions of those stiffnesses to quite low values (indicating a significant volume fraction of crack phase as the fracture strain of the specimen is approached). These stiffness reductions are nonlinear functions of the applied stress field, to be sure, but they are monotonic and related to the

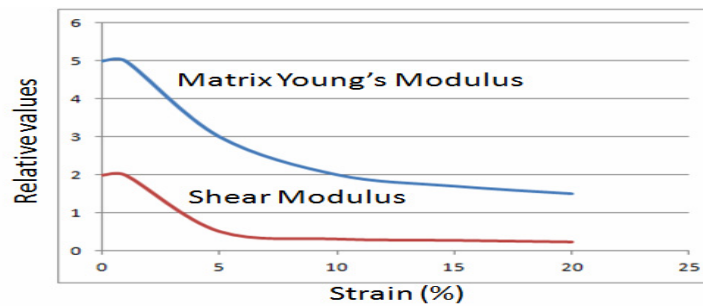global compliance of the specimen in a relatively straightforward way.

Fig. 5. Change in matrix-dominated lamina Young's modulus and shear modulus required in classical laminate analysis to maintain the engineering stiffness required as a function of applied strain to create the specimen response measured in Fig. 4

Recently the authors have created a broadband dielectric spectroscopy (BbDS) method of measuring the dielectric permittivity of such a specimen in-situ during a continuous loading to failure of such specimens (More will be said of this method in a subsequent publication). The data to be considered in this paper are produced by the uniaxial tensile loading of coupon specimens of woven glass fiber reinforced epoxy loaded in an off-axis direction. Strain was measured with an extensometer and concomitantly the permittivity was measured at a fixed frequency of 10 Hz by a Novocontrol unit using specially designed plates fixed on opposing sides of the thickness of the specimen. An example of the data obtained in such a test is shown in Fig. 6. The stress–strain response for this 45° off-axis test is quite nonlinear and shows a large strain to break, of about 14%. A transition region of strain from values of about 1 to 5 percent is clear in Fig. 6, during which time the rate of stress increase per unit strain increase is sharply decreasing. That region in Fig. 5 shows a sharp decrease in matrix stiffness, and can be associated with the initiation of microcracks in the matrix material. During the remainder of the extension, the changes in the stress strain curve in Fig. 6 and the matrix stiffness changes in Fig. 5 are much smaller than the initial period.
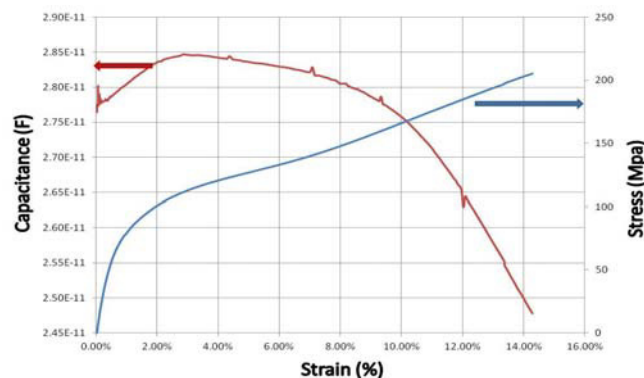

Fig. 6. Capacitance (effective permittivity) of a woven continuous glass fiber reinforced epoxy specimen as a function of nonlinear stress / strain response.

The changes in the total permittivity of the specimen, measured as the capacitance, are also shown in Fig. 6. These results are quite remarkable, since the values initially rise in the early (crack initiation)

phase of the elongation, and then monotonically decrease. This unexpected (and previously unreported) result is exactly the behavior predicted by our closed form analysis for non-dilute mixtures of a "matrix" of glass/epoxy with an increasing "second phase" of microcracks (as shown in Fig. 3) when the matrix has a higher dielectric permittivity and lower conductivity than the crack phase (values given above). In the present physical case, the glass/epoxy specimen has near-zero conductivity and large permittivity. When cracks begin to form, they have the nominal properties of ambient air, i.e., lower permittivity than the glass/epoxy (by a factor of about 5) and slightly better conductivity (due to a finite relative humidity). But our closed form harmonic solutions to Maxwell's equations show that the effective permittivity of the constituent phases, given in Eq. (1), depend on both the conductivity and the real part of the permittivity of the materials. Moreover, for low frequencies, as shown in Eq. (1), the effect of even a small value of conductivity can be substantially large. When small volume fractions of crack phase are introduced, this effect initially increases the collective permittivity of the specimen, as predicted. As cracks accumulate to occupy a larger volume fraction of the material, since the permittivity of that crack phase is quite small compared to the glass/epoxy phase, the collective specimen permittivity decreases, most sharply when the crack volume fraction becomes large, as shown in Fig. 6 and predicted in Fig. 3.

It should be emphasized that these changes in permittivity and conductivity are distinct and measurable changes in material state, and that they are caused by a non-conservative material response to the applied fields. It should also be emphasized that the analysis predictions do not have adjustable constants; they depend only on constituent properties and defect characteristics and can be compared to direct measurements of the permittivity of the constituents and heterogeneous material.

5. Conclusions and directions

The present paper introduces a new multiphysics concept of generalized compliance which is applied to the interpretation of changes in state of a heterogeneous material under the combined application of mechanical and electrical fields. It is shown that the electrical compliance, measured and calculated as the dielectric permittivity in the present example, is remarkably sensitive to both the conductivity and permittivity of the individual constituent phases (independently) in a heterogeneous material, including those of the defects introduced during changes in material state. Moreover, the permittivity is capable of providing information that can discriminate different mechanisms of non-conservative changes in state, defect initiation and accumulation leading to failure in the present case. Finally, changes in electrical compliance is sensitive to the shape, size, orientation, and volume fraction of crack phases introduced during mechanical loading, and those changes can be uniquely calculated and predicted as a function of the mechanisms that produce them.

These new features present many opportunities, especially for heterogeneous mixtures which are inherently dielectric. As a detector of degradation associated with micro-damage, for example, since we calculate absolute values of permittivity as a function of both the intrinsic and extrinsic characteristics of all of the phases of the material, explicitly and exactly, the generalized compliance method provides a new assessment method for the evolution of properties and performance of heterogeneous materials. Also, since changes of state of the material can be directly and uniquely reflected in the changes in generalized compliance, one can construct a prognosis of material behavior when future applications of fields over time and history of loading are simulated. Of course, many of these opportunities are yet unexplored. However, the multiphysical foundations for these investigations are sound.

These characteristics are of special value to the design of heterogeneous functional materials for energy systems such microstructures for fuel cells, capacitors, batteries and separation membranes. Many of these and other such devices involve materials that have significant ionic as well as electrical conduction, i.e., they are "mixed ionic and electronic conductors" or MIECs. Indeed, those materials are often

heterogeneous and the ionic and electronic conduction can be "designed" by careful selection of the constituent materials, and design of their microstructures. In some cases, the purpose of that design is specifically to store energy, in which case the permittivity discussion above is directly applicable. However, for nearly all heterogeneous materials, the generalized compliance method is a guide to the design, processing, and assessment during service of such material systems to follow the evolution of microstructures and properties, and to construct a prognosis of future functional response.

Acknowledgements

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