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MECHANICS OF COMPOSITE MATERIALS IN FUEL CELL SYSTEMS

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The science and technology that are fundamental to the concept of composite materials are also the foundation for the construction and function of fuel cells and fuel cell systems. The present paper outlines this relationship in the context of the physics and chemistry that are enabled by the specific selection and arrangement of constituents of the “functional composite” fuel cell. General principles of operation are described, and fundamental issues are defined that must be addressed by the composites community if the fuel cell science and engineering is to advance. Examples of several types of functional composite fuel cells are presented, with emphasis on polymer electrolyte (PEM) and solid-oxide (SOFC) systems. Specific needs for continued research are identified.

Fuel Cells as Composite Material Systems

Fuel cells are electrochemical devices that convert chemical energy into electrical energy and heat. They are unique at the fundamental and technical level and offer unique advantages to society, such as greater energy conversion efficiencies and little or no production of noxious by-products. Because of these features, nearly every country has a national initiative to develop fuel cells and fuel cell systems. That development involves overcoming numerous technical barriers to reduce the cost, determine the durability, and improve the performance of fuel cells. Much research is being done with those objectives. The present paper addresses a part of that research that is concerned with developing an understanding of fuel cells as functional composite materials, with special attention to the technical problems which involve mechanical response in some way.

The basic principle of operation of a fuel cell, in general, is illustrated by the schematic in Fig. 1. We will discuss a fuel cell that operates with hydrogen and oxygen as the active elements, although there are, of course, other choices for reactants. For two or more reactants that would like to form a compound, an electrochemical potential will exist between the ionic forms of those reactants. In a fuel cell, the reactants, oxygen and hydrogen ions in our example, are separated by an electrolyte which is an electrical insulator, so an electrical charge (potential) develops across the cell, as suggested in Fig. 1. If the electrolyte is chosen so that ions of one of the reactant species are conducted through that layer, then an electrical circuit can be completed by connecting the outside layers of material of the cell (the electrodes, which are electrical conductors), and the electrical potential will provide power to the external electrical load. In this way, the (Gibbs free) energy that drives the chemical reaction can be converted to electrical power, rather than given up entirely as heat, as would happen if the reactants were simply combined. But

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Fig. 1. Schematic diagram of a generic fuel cell as a composite material system: 1 — fuel; 2 — anode; 3 — catalyst layers; 4 — cathode; 5 — air/oxygen; 6 — electrolyte; 7 — load.

some heat is produced by the fuel cell as well, since we must create the ionic form of the constituent reactants, transport them in the ionic as well as gaseous (or liquid) form, and conduct electricity to achieve the process just described.

Returning to Fig. 1, we see a catalyst layer on either side of the electrolyte. The general function of those layers is to convert the gases or liquids supplied to the fuel cell into ionic reactants. These electrochemical reactions in a general form are

at the cathode,

at the anode, and

for the overall fuel cell reaction.

So, in the case of oxygen, for example, the catalyst adsorbs the species onto its surface, the oxygen diffuses over the surface to a location where it can find two “extra” electrons (which have been transported through the external circuit and conducted to that location) to become an ion (O^{2-}) and travels through the ionic conductor (electrolyte) to the anode, where it combines with hydrogen to form water (for the case where the electrolyte conducts oxygen ions). If the electrolyte conducts protons, the hydrogen ions are conducted to the cathode, and the water is formed there. The process just described requires the presence of “triple points,” which can be reached by the gaseous carrier of oxygen or hydrogen (for this example), the electrons, and the ions involved in Eqs. (1)-(3). These triple points or triple-point boundaries are geometric constraints on the type of composites which we can create for this system. Transmitting the gasses (or fluids) requires porosity (with specific features), and the porous materials must be in contact with ionic and electrical conductors, or they must be a composite made of ionic and electrical conductors to create the triple-point regions which make the electrochemistry work. But the outermost layers of the fuel cell must be electrical conductors, since they must transport electrons from one side of the cell to the other. In fact, not shown in Fig. 1 are “current collector” layers or “bipolar plates” for the stacks of cells which collect the current and seal the activity of one cell from another.

This functional composite system must support all of the activities just described at different temperatures and pressures, and the different layers must be sealed and insulated from one another, since any leakage of one reactant to another

Fig. 2. Stress–strain response σ – ϵ of a commercial PEM membrane material under quasi-static loading in the machine direction (—) and in the perpendicular direction (- - -).

means a loss of voltage and current in that region and an increase in heat. Electrical shorts also decrease the performance for the same reason. In fact, sealing the fuel cells is one of the most difficult engineering problems to solve. Polymer-based fuel cells, like PEM systems, typically operate in the 80-100°C range, but solid-oxide systems (SOFCs) typically operate in the 800-1000°C range. Sealing a system at those temperatures is a great challenge.

Static Requirements and Failure Modes

From the previous discussion, it is clear that the constituent materials in a fuel-cell composite material system must be chosen very carefully so that they be able to act and interact in a precise manner to make the fuel cell work. Indeed, this is a composite in the most fundamental sense, in that the constituents act and interact in such a way that their function and character together is dramatically different from any simple sum of their characteristics. It is clear that the design of this functional material system is a composites problem.

Indeed, the electrochemical requirements dictate and constrain many of material constituent choices and limit others. For example, PEM electrolytes, or membranes as they are called, must conduct protons efficiently, with a minimum of ohmic loss as heat. Hence, they are typically made from special combinations of ion-conducting polymers, called ionomers, which operate in a hydrated condition. In fact, these materials may change their physical dimensions by an order of 20 percent during such hydration, which makes the job of sealing the cell challenging. Moreover, the hydrated membrane must maintain its mechanical integrity; if it ruptures or leaks, the fuel cell will fail to operate. The membrane is typically subjected to an out-of-plane pressure, sealing pressure, and in-plane displacements caused by changes in temperature, hydration, and the manufacturing process of sealing the cell. So, the mechanical response of the membrane is very important. Moreover, if the mechanical situation in the fuel cell is to be modeled, the constitutive behavior of the membrane must be known as an input to analysis methods such as discrete-element codes.

However, the mechanical behavior of PEM membranes is quite unusual. Figure 2 shows an example of the stress–strain behavior of a commercial polymer membrane material under various conditions. It can be seen that the behavior is highly nonlinear and that the strain to failure of the materials is typically more than 100 percent. As it happens, the behavior is also essentially elastic-plastic, i.e., there is relatively little strain-rate dependence in the response. Finally, the membrane may be anisotropic. The “machine direction” (MD) exhibit a considerably different response than does the material when loaded in the direction transverse to the machine direction, “TD,” as indicated in the figure.

Figure 3 shows the stress–strain response of an assembly such as the one illustrated in Fig. 1 for a polymer (PEM) system, compared to the response of the membrane alone. The catalyst and diffusion layers have added some rigidity to the re-

Fig. 3

Fig. 4

Fig. 3. Relations between the normalized stress σ_n and the normalized strain ϵ_n for a commercial membrane electrode assembly (MEA) (1, 2) and the membrane (3, 4) under quasi-static loading in the longitudinal (1, 3) and transverse (2, 4) directions.

Fig. 4. Local structure of a ceramic fuel cell (after S. Majumdar, et al., reprinted with permission of The American Ceramic Society (ACS), PO Box 6136, Westerville, OH, 43086, copyright 1986, ASC, all rights reserved).

sponse noted in Fig. 2, but they have also changed the basic nature of that response. There is now a distinct “yield behavior” observed, followed by a region of nearly uniform stress as a function of increasing strain. The total strain to failure is also different. Even though the porous layers have a very low rigidity themselves, they alter the composite response significantly.

Figure 4 shows a scanning electron micrograph of the cross section of a ceramic fuel cell, taken from the literature. For this high-temperature fuel cell, the constituent layers are typically oxides or cermets. The cathode and anode layers are porous, and they catalyze the reactant gases. In the case shown, there is a composite region in the cathode which is a composite of the cathode material and the electrolyte, to create triple-point boundaries, as discussed above. The anode is a composite as well, consisting of Ni as an electronic conductor and a YSZ compound as an ionic conductor. Figure 5 shows a micrograph of the anode at a much higher magnification. It can be seen that there it is a composite with several distinct constituents and that they create triple-point boundaries with the porous cavities, as required for the electrochemical reactions. It should be mentioned that, at present, these composites are made based on very specific choices for the materials involved, considering their electrochemical efficiency, thermal stability, and compatibility. However, the specific shapes, sizes and geometric arrangements are functions of processing, and they are not optimized against the governing equations which describe the physics, chemistry, and mechanics of the local situation. This is a challenge and a great opportunity for the future.

One of the most difficult requirements to achieve for the SOFC composite (and other high-temperature systems) is the thermal compatibility. Ceramic composites are typically processed at very high temperatures, above 2000°C in some cases. When the fuel cell is not operating, it may be at ambient temperature. Thus, the different material layers may have to remain bonded together and maintain their integrity over a change in temperature of more than 2000°C. Also, the thickness of individual layers may be only tens of microns, and some of the layers may be much thicker than others. Figure 6 illustrates some of the calculated stresses that occur in such systems for typical materials used [1]. At least two failure modes can be driven by these stresses. The first is cracking of the plies. These through-thickness cracks are driven by differences in the ply-level stiffness and

Fig. 5. SEM micrograph of the anode region of an SOFC.

thermal expansion coefficients (which would produce a different in-plane deformation for each ply as a function of temperature change if the plies were not bonded together).

But Fig. 6 also shows a tendency for another failure mode if different material property mismatches are selected. If the dense electrolyte has a smaller coefficient of thermal expansion than the electrode layers on either side, for example, as the fuel cell cools down from the manufacturing temperature, tensile stresses through the thickness of the composite (interlaminar stresses) develop near the edges of the fuel cell (top right of Fig. 6). These stresses can drive delamination in those regions. This delamination may be a minor mechanical defect, but it causes total failure of the fuel cell in that region, since the layers must be in contact to conduct ions and electrons. If the electrolyte is in tension upon cooling, cracking may occur (top left in Fig. 6). And if the interconnect region contracts more than the fuel cell during cooling, buckling of one or more of the fuel cell components may occur, as shown in the bottom right of Fig. 6. Finally, there is a combined failure mode associated with this discussion. As it happens, local delaminations are quite often driven by ply cracking in layered composites. [2] Hence, if a crack forms in one of fuel-cell material layers, it is quite likely that delamination will form at the tips of the cracks and will grow along the material interfaces to cause local regions of failure.

For polymer-based fuel cells, water is often involved in the transport of protons. As we have mentioned, hydration greatly affects the properties of the constituents and causes significant changes in the volume of ionomers in the membranes. In that sense, water in those systems plays the role of temperature in ceramic systems from the standpoint of causing a relative local motion between constituent layers. And this brings us to one last general point. Neither the temperature in an SOFC nor the hydration in the case of a PEM cell is entirely uniform throughout the fuel cell. Typically, there are variations of temperature or hydration in the plane of layers as well as through the thickness. Hence, differential pointwise motion of local material points is to be expected and can be a source of damage or failure.

Functional Failure Modes

For functional composite fuel cell systems, the loss of mechanical integrity is only one of many failure modes. Any loss of function of the composite can cause failure of the fuel cell. A full discussion of this subject would require a complete description of that functionality, based on a robust representation of the multiphysics processes which make a fuel cell work. Numerous such representations, with various measures of robustness, are available in the literature [3-5]. For present purposes, we will refer to the recent model of a tubular SOFC developed by the authors. As a first example, we return to the question of porosity. The porosity in an SOFC may change in size and shape as a function of operating conditions of the fuel cell and the constituent materials involved. Figure 7 illustrates a consequence of this change. The influence of porosity on the performance is treated as a combination of two contributions: (1) gas transport, through the effective diffusion coefficient, which is a function of Ψ (Ψ = porosity ε / tortuosity τ); (2) charge transport resistance inside the composite cathode, through the effective charge

Fig. 6. Calculated thermal stresses σ_t in the layers of an SOFC as functions of CTE mismatch of constituents.

Fig. 7. Change in the conductivity γ of a mixed conductor cathode and the corresponding current density j as functions of changes in the porosity ε during operation of a mixed conducting SOFC.

transfer resistance parameter. Physically, in the high-porosity regime, although the higher partial pressure of oxygen can drive the reaction forward, lesser ionic paths will increase the oxide ion density in the crystal lattice that drives the reaction in the re-

Fig. 8

Fig. 8. SEM micrograph of a catalyst layer in a PEM cell, showing Pt particles on carbon particle carriers in an ionomer matrix.

Fig. 9

Fig. 9. Schematic diagram of typical changes in the resistivity of bulk material and interfaces in ceramic fuel cells. 1 — bulk material; 2 — interface material; 3 — cell performance.

versed direction, which is described as the ambipolar conductivity characterizing the simultaneous properties of effective electronic and ionic conductivities in a mixed conducting oxide cathode.

Here we see that a change in a material characteristic may decrease or increase the functional performance of a fuel cell, depending on the net effect on the multiphysics involved. In the cathode, for example, an increasing porosity size reduces the resistance to flow of reactant gas (for our SOFC example), which tends to increase the performance, but it also reduces the available locations for triple-point boundaries, which tends to decrease the performance because of the reduced conductivity. The point to be made is that there is a best case for this composite design, which must be determined from a comprehensive analysis and proper interpretation. No single-variable design or heuristic design process is likely to produce an optimum composite for this purpose.

Another example of functional changes in a ceramic fuel-cell composite system has to do with transport of materials in a PEM system. Figure 8 shows a scanning electron micrograph of a catalyst layer (schematically illustrated in Fig. 1). The darkest points are Pt particles, which are the catalyst in this case. Those particles are carried by larger carbon particles, which appear as shaded regions in the micrograph. The surrounding material is an ionomeric polymer, the ionic conductor. The triple-point region is created by the gas adsorbed on the Pt in contact with the electronic conductor (carbon) and the ionic conductor (polymer matrix). However, as the SEM shows, the Pt particles are very small and have a very large surface to volume ratio. So they tend to agglomerate as the reactants are transported through the catalyst region. We have measured considerable changes in the particle size and distribution.[1]

Migrations of various other types are also of concern in fuel cell systems. Material interfaces are often greatly affected by such behavior. Figure 9 shows a schematic example of a typical result for ceramic systems. Bulk materials in such systems may densify with time at a temperature, decreasing the ionic or electrical resistivity. However, interfaces may degrade by compound formation [6], by the loss of electrical contact due to densification, or by the accumulation of vacancies or contaminants. Consequently, the resistance of the interfaces may increase while the resistance of the bulk materials is decreasing. If the rates of those two behaviors are different (a common occurrence), the performance of the fuel cell may increase at first and decrease later (also common), or vice versa.

Conclusions and Continuing Directions

Fuel cells are functional composite material systems; the science and technology that are fundamental to the concept of composites is at the base of how and why fuel cells work. That science and technology is highly multidisciplinary and typically involves multiphysics processes (thermal, chemical, mechanical, and electrochemical) that are highly coupled and often nonlinear. Analytical representations of those processes are typically effected by dividing the fuel cell into specific (composite) layers as regions or zones and writing constitutive and balance equations that are matched to boundary conditions at the interfaces of the regions. Transfer coefficients, source terms, and sink terms are often incorporated into those boundary conditions. While these formulations are quite useful in a conceptual design, they do not specifically address the local characteristics of the composite materials involved and rarely consider the coupling between mechanical and chemical activities, for example. Involvement of the composites community in this enterprise is greatly needed. In this short space, only a few specific needs are listed below:

1. Established composite design and analysis methods should be more fully utilized to address the design, manufacturing, aging, durability, and reliability of fuel cells and fuel cell systems.
2. These analyses should be supported by measurements of local composite properties in fuel cells, especially the constitutive characteristics (as functions of temperature, hydration, and other extensive variables as appropriate) into the nonlinear range if needed, interface properties (including transfer characteristics), and microstructure. Moreover, these measurements should be done as functions of history of fuel cell operation in order to enable science-based durability and reliability analyses, to replace the parametric and heuristic methods currently used.
3. Science-based composite analyses should be properly set and performed for a variety of local problems, such as the design of triple-phase regions (as shown in Fig. 5), to replace the manufacturing expediency with technical rigor in our efforts to optimize fuel cells.
4. Robust modeling, assisted by experiments, should be used for constructing systems-to-science design methodologies to replace the current Edisonian design-fix-fail methods currently used to bring fuel cells to applications in society.

A purpose of this paper is to solicit the assistance of the composite materials community in achieving these and other goals in bringing functional composite material systems such as fuel cells to the benefit of society.

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