Modeling of Chemical-Mechanical Couplings in Solid Oxide Cells and Reliability Analysis

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Abstract

Solid oxide fuel cell (SOFC) has been well demonstrated as a promising clean energy conversion technology. Long-term stability is an important requirement for practical applications of such a technology. Nevertheless, very aggressive operating conditions, e.g., high temperatures (600–1000°C) and extremely low oxygen partial pressures (anode electrode), generally lead to various degradations of SOFC material systems, which seriously impede the deployment of SOFC technology. It is therefore essential to increase the understanding of fundamental SOFC degradation mechanisms. The basic structure of SOFCs is a positive electrode-electrolyte-negative electrode (PEN) tri-layer assembly, in which the dense electrolyte is sandwiched by porous electrode on either side. Because the material is different from one layer to another in PEN structure, and different materials have different thermal expansion coefficients, thermal stress occurs in PEN structure at elevated temperatures. The thermal stress effects on SOFC structures have been investigated extensively in open literature. However, it is difficult for thermal stress analysis alone to interpret some of the degradation phenomena associated with PEN structure reliability issues, such as delamination at oxygen electrode/electrolyte interface. Typical SOFC materials are ionic-conducting and mixed-ionic-electronic-conducting ceramics. These materials have the ability to release and store oxygen in addition to a high concentration of oxygen vacancies for high oxygen ionic conductivity. The oxygen vacancies are generally created through appropriate doping and significantly affected by non-stoichiometry conditions. The oxygen vacancies displace atoms from their ideal locations in intrinsic crystal structure, leading to very complicated chemical-mechanical coupling phenomena in SOFCs, which could have significant effect on the reliability of SOFCs.

The research in this dissertation is aimed at studying the chemical-mechanical couplings and their effect on reliability of SOFC structure. A micro model is first developed based upon the rigorous theory of chemical-mechanical coupling relating defect (e.g., oxygen vacancy) transport process in conducting ceramics with solid mechanics. The model is used to investigate the stresses at cathode/electrolyte interface and highlight the different mechanisms of chemical and thermal stresses. The results indicate that both the chemical stress and thermal stresses are complicated at the cathode/electrolyte interface; the chemical stresses show different distribution patterns from the thermal stresses. The thermal and chemical
stresses can be partially canceled out with each other, leading to the reduced overall stresses at the cathode/electrolyte interface. The distributions of oxygen partial pressure and thus the oxygen vacancy concentration on the cathode particle surface have significant effects on chemical stress distributions and consequently on the principal stresses at the cathode/electrolyte interface.

Since the defect transport process in conducting ceramics and non-stoichiometric conditions are closely related to the multi-physicochemical processes in SOFC devices, the multi-physicochemical modeling is also developed, linking multi-physicochemical processes with measurable electrochemical performance of SOFCs, whereby the chemical-mechanical couplings under complicated multi-physicochemical conditions is studied. The model is validated using experimental polarization curves, upon which systematic simulations are carried out. Results show that the peak value of the first principal stress occurs within the anode electrode and at the cathode/electrolyte interface; the third principal stress shows a peak value at the cathode/electrolyte interface. The chemical stress particularly the peak values of the first and third principal stress can be mitigated by increasing the cell operating voltage (i.e. decreasing cell current). The hydrogen molar fraction in the fuel shows slight effect on chemical stress. The porosity of electrodes shows significant effects on chemical stress. Bigger porosity can significantly decrease the extremes of the first and second principal stresses in PEN assembly. The effect of electrode tortuosity is negligible on chemical stress. Larger anode thickness in the anode-supported SOFCs increases the chemical stress in the anode electrode but favors decreasing the chemical stress in electrolyte and cathode domain. The Weibull analysis shows that high cell operating voltage and low hydrogen content in the fuel may mitigate failure probability of PEN assembly. With relatively low electrode porosity, the anode electrode is a vulnerable component in the anode-supported button cell; with relatively high electrode porosity, the electrolyte and cathode layer become vulnerable components. Large anode thickness can mitigate failure probability of electrolyte and cathode layer but increase anode failure probability. The failure probability is not sensitive to the thickness variations of electrolyte and cathode layers. Relatively thinner anode and cathode, and thicker electrolyte as well as high operating cell voltage can reduce the elastic energy stored in the cathode layer and therefore mitigate the probability of delamination failure at the cathode/electrolyte interface in anode-supported SOFCs.

Electrochemical impedance spectroscopy (EIS) techniques have been widely used for conducting ceramics and SOFCs. The part of research activities is also focused on the study of mixed ionic electronic conductors (MIECs) using EIS technique. In particular, the EIS model is developed, linking defect transport process in MIECs to EIS response. The EIS model is used to interpret the EIS data of MIECs under different stress state. The complicated coupling mechanisms are elucidated between defect transport processes in grains and grain boundaries and associated stress state.