Electrochemical Measurements on Cells, I: Simulation of Potential Distribution with an Embedded Probe

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Measurements of electric potential in electrochemical devices such as solid oxide fuel cells (SOFC) or solid oxide electrolyzer cells (SOEC) are often made by placing a reference electrode on the surface. Measurement of electric potential with embedded electrodes (probes) has also been reported [1]. In a typical SOFC, it is assumed that the electronic conductivity is negligible compared to the ionic conductivity. The establishment of local thermodynamic equilibrium, an assumption made in virtually all transport theory, requires that the electronic conductivity cannot be set to zero mathematically [2,3]. Thus, to elucidate the role of electronic conduction in a predominantly ionic conductor, it is necessary to incorporate the electronic conductivity. Also, local equilibrium demands that transport of both ions and electrons (holes) be taken into account to describe the local chemical potential of electrically neutral species, such as oxygen. The local chemical potentials of electrically neutral species determine the thermodynamic stability and thus also the device stability.

The purpose of the present work was to calculate distribution of electron electrochemical potential, oxygen ion electrochemical potential and oxygen molecular chemical potential inside a typical solid electrolyte used in an SOFC or in an SOEC.

Two typical cell geometries are considered in the simulation: one is an anode-supported cell (Fig. 1A); the other is an electrolyte-supported cell (Fig. 1B). These cells were simulated under both a fuel cell mode and an electrolysis mode.

Potential distribution for both electrons and oxygen ions obey Laplace equation, equation 1 and 2, respectively, assuming the ionic and the electronic conductivities are position independent. Interfacial regions are described by a set of transport properties and interface thicknesses. Local chemical equilibrium is described by equation 3.

$$\nabla(\sigma_e \nabla \mu_e) = 0 \qquad (1)$$

$$\nabla(\sigma_i \nabla \mu_i) = 0 \qquad (2)$$

$$\frac{\mu_{O_2}}{4e} + \phi = \frac{\mu_{O^{2-}}}{2e} \qquad (3)$$

The σ's are the conductivities, the μ's are the chemical potentials, and the ϕ is the measurable electric potential. Simulations were performed using both two dimensional and three dimensional finite element analysis (FEA). Fig. 2 shows the sample meshing used. Fig. 3 shows the simulation results for different parameters. The simulation results lead to a conclusion that, in order to measure potential distribution inside cells, embedded metal probe coated with electrically insulating shell should be used.

References:
1. Lim H.T., Virkar A.V., Journal of Power Sources, 192, 267 (2009)
2. Virkar A.V., Journal of Power Sources, 147, 8 (2005)
3. Virkar A.V., International Journal of Hydrogen Energy, 37, 12609 (2012)
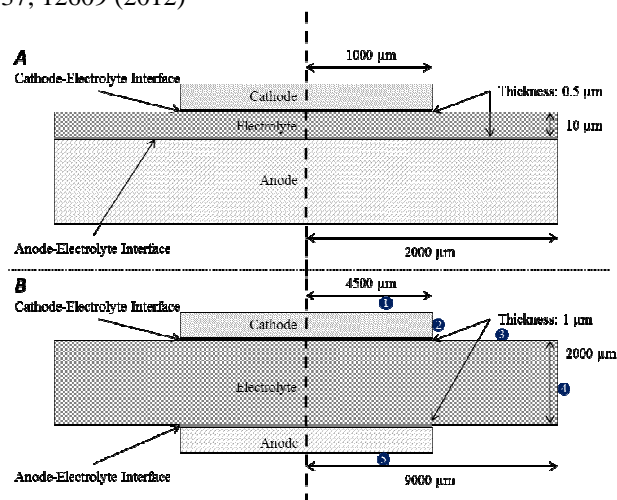

Fig. 1A shows an anode supported cell; 1B shows an electrolyte supported cell. Interface regions were modeled as very thin layers exhibiting both ionic and electronic conduction.
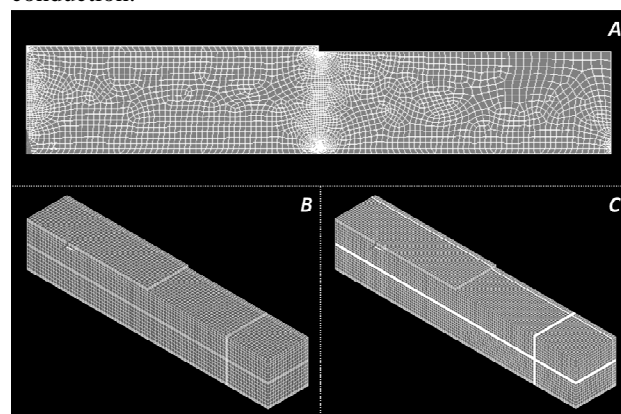

Fig. 2 Both 2D and 3D FEA simulations were conducted. A shows a 2D meshing for sample without a probe; B shows a 3D sample with an embedded metal probe; C shows a 3D sample with an embedded metal probe coated by an insulating shell.
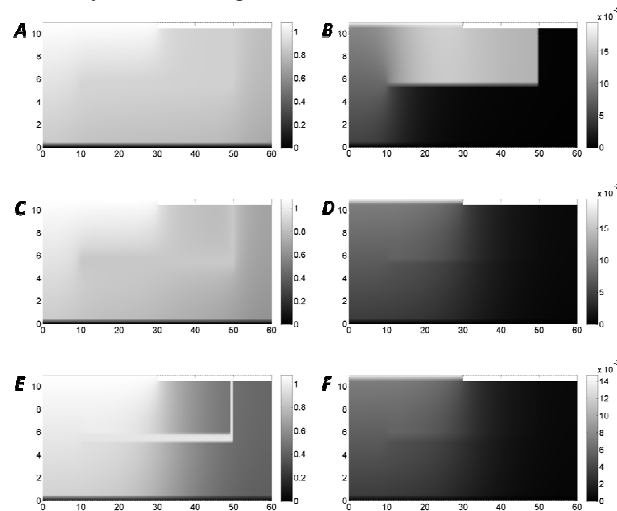

Fig. 3 Electronic and ionic electrochemical potential distributions inside the cells are shown. E shows that embedded probe with an insulating shell is the best option to measure electronic electrochemical potential without interference.