ABSTRACT

The present dissertation explores the effect of non-idealities on the interfacial processes in a solid oxide fuel cell and Li-ion battery. Broadly, cation interdiffusion in a SOFC and diffusion-induced stresses in the solid electrolyte interphase layer (SEI) in a Li-ion battery are investigated. Two important non-idealities namely, the finite size of ions and the temperature difference across the interface are considered during cation interdiffusion in SOFC. Similarly, in the Li-ion battery, the effect of the heterogeneity of the SEI layer and cell temperature on diffusion induced stresses in a silicon anode particle is considered. In the first problem, the effects of the finite size of ions (the most often-used idealization being that ions are treated as point charges) on cation interdiffusion across the electrode-solid electrolyte interface are studied using a detailed mathematical model. A phase-field model is used to couple the properties of the electrode and electrolyte, appropriately accounting for the diffusivity matrices, lattice constants, tracer diffusion coefficients of the solid electrode (strontium-doped lanthanum manganite (LSM)) and the solid electrolyte (yttria-stabilized zirconia (YSZ)) and so on. The finite size of the ions is taken into account through a modification of the chemical potential of the ions. The consideration of this non-ideality has a major effect on the interdiffusion length (IL) of the cations and electric potential at the electrode-end away from the interface.

In the second problem, the combined effect of the temperature difference across the interface and the finite size of ions is studied on cation interdiffusion. Two criteria are suggested: one for the selection of the proper domain length to perform simulations, and the other for the determination of the IL for each cation. The diffusive flux of ions is derived based on the formalism of irreversible thermodynamics. The temperature of one phase (LSM) is kept constant while that of the other phase (YSZ) is varied to obtain a larger temperature difference across the interface. The effect of the temperature difference across the interface and the finite size of ions on cation interdiffusion is investigated both in a combined way and separately after implementing both criteria. The difference in the ILs and the electrical potentials at the electrode end (with and without considering these effects: the temperature difference across the interface and the finite size of ions) are deduced.

In the third problem, a systematic procedure is proposed to determine the model parameters (gradient energy coefficient and height of double-well potential) for the phase-field method which is used to study cation interdiffusion in the first two problems. The model is adapted from solidification studies and is based on two important limits: sharp and thin interface limits. The phase-field model parameters are determined under both the interface limits. The maximum interface thickness is determined based on the thin interface limit. Further, a variation of the interfacial energy is also performed to determine its effect on cation interdiffusion. The reason behind the nature of variation of IL is explored under the thin interface limit for various values of interfacial energy.

In the fourth problem, the effect of heterogeneity of the SEI layer along with the cell/battery temperature on the chemo-mechanical stresses in a silicon anode particle during lithiation/delithiation is investigated. The effect of temperature on the radial and hoop stresses in the particle without the SEI layer is also presented. Further, the radial and hoop stresses obtained for the heterogeneous SEI layer are compared with those of the homogeneous SEI layer to demonstrate the importance of the heterogeneity of the SEI layer. Two major influences on peak hoop stress generated in the SEI layer are studied: first, the influence of the thickness of the SEI layer relative to the particle size; and, second the influence of the material properties – in particular, the relative magnitudes of the elastic moduli of the inorganic to the organic portion of the SEI layer also the Poisson's ratio of the SEI layer and the silicon particle. The effect of the cell temperature along with the aforementioned parameters is also investigated on the peak hoop stress in the SEI layer. The effect of the cell temperature is discussed in terms of the differences in the stresses obtained with and without temperature variation. It is expected that the present work will provide an initial base to investigate the effect of the non-idealities on the interfacial processes in the SOFC and Li-ion battery, and contribute, more generally, to future investigations of other electrode-electrolyte combinations. Further, it is expected that the heterogeneity of the SEI layer studied here may contribute to the improved estimation of failure criterion of this layer under different modes such as fracture, delamination, and debonding, and will ultimately help in the development of robust and stable artificial SEI layers/functional gradient layers to increase the life and performance of the Li-ion batteries.