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## BESH2017 Thermodynamic, Kinetic and Electrochemical Studies on Mixed Proton, Oxygen Ion and Electron (Hole) Conductors

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### Program Scope

The principal objective of the work is to conduct thermodynamic, kinetic and electrochemical studies on mixed proton, oxygen ion and electron (hole) conductors. Transport processes are analyzed using linear non-equilibrium thermodynamics. Onsager coefficients including cross terms in coupled transport are determined. Transport processes in fuel cells, electrolyzers, reversible cells, and lithium batteries are examined using linear non-equilibrium thermodynamics. The role of low level electronic transport on chemical potentials of electrically neutral species is assessed. Relative directions of ionic and electronic flows determine whether or not chemical potentials within the electrolyte are bounded by the electrode values. The relative directions of ionic and electronic currents determine the sign of the Onsager non-diagonal terms ( $L_{ij}$  where  $i \neq j$ ). That is, in mixed proton–oxygen ion–electron/hole conductors through which  $H^+$  and  $O^{2-}$  ions transport and effectively hydrogen ( $H_2$ ) and oxygen ( $O_2$ ) are transported, the sign of  $L_{H_2O_2}$  is dictated by the relative directions of ionic and electronic currents. If the ionic and the electronic currents are *anti-parallel*, the  $L_{H_2O_2}$  is positive. If the ionic and the electronic currents are *parallel*, the  $L_{H_2O_2}$  is negative. It is shown that if the ionic (e.g.,  $H^+$ ,  $O^{2-}$ ,  $Li^+$ ) and the electronic currents are *parallel*, the chemical potentials of the corresponding neutral species ( $H_2$ ,  $O_2$ , lithium(Li)) in the electrolyte can exceed electrode values. This can lead to either electrolyte reduction or precipitation (and pressurization) of neutral species ( $H_2$ ,  $O_2$ , Li) and failure of the electrochemical devices. Thermodynamic stability of electrochemical devices such as fuel cells, electrolyzers, lithium ion batteries is examined.

The experimental part involves the use of alternating current and direct current techniques to investigate transport properties (Onsager transport coefficients, ionic and electronic conductivities) and a study of local thermodynamics by embedded probes. Using these techniques, spatial distributions of chemical potentials of electrically neutral species ( $H_2$ ,  $O_2$ , Li) inside an electrolyte are calculated and measured. The role of coupled transport is also examined in the stability of proton exchange membrane fuel cell (PEMFC) cathodes. The thermodynamics of catalyst–support interaction are examined both theoretically and experimentally. This examination includes a study of electrochemical Ostwald ripening of platinum-based nanocatalysts and the role of the catalyst support. Ostwald ripening of PEMFC catalysts thus involves transport of two charged species ( $Pt^{2+}$  ions and electrons), through two different phases.

Many transport processes can be formulated within the linear non-equilibrium thermodynamic framework (Onsager equations), in which the departure from thermodynamic equilibrium is assumed to be small. However, if the assumption of small departure from equilibrium is not valid, then the description of local thermodynamics requires the use of nonlinear non-equilibrium thermodynamics. If a system is sufficiently far away from thermodynamic equilibrium, oscillatory behavior may be observed.

Determination of whether oscillatory behavior can be observed in all solid state systems is of particular interest.

## FY 2016 Highlights

- A parametric equation describing polarization in solid oxide fuel cells (SOFCs) in terms of experimentally measurable parameters was developed. The equation explicitly describes activation and concentration polarizations at the two electrodes and the ohmic loss as functions of current density. Using known values of parameters measured on cell materials and components, various polarizations are estimated as functions of current density and the possible performance characteristics are assessed. The calculated performance curves using measurements made on cell materials and components are in good agreement with actual fuel cell tests. Using the model, prospects for ultra-high power density SOFC at intermediate temperatures ( $<800^{\circ}\text{C}$ ) are examined. The results show that even in thin electrolyte film anode-supported cells, the ohmic contribution can be substantial, not all of it being attributable to electrolyte and electrode materials. The results also show that the electrode particle size has a substantial effect on the activation polarization. A manuscript based on this work was published in the *Journal of Power Sources* (2015).
- A new oxygen permeation (transient) technique was developed to measure the electronic conductivity of yttria-stabilized zirconia (YSZ). The permeation cell is a YSZ disc with an embedded Pt probe and a cavity at the center. Two porous platinum (Pt) electrodes are applied on the disc surfaces. By applying a small DC bias across one surface electrode and the embedded probe, oxygen is pumped into the disc and stored in the cavity. In steady state, a stable Nernst potential is developed between the cavity and the outer surfaces. When the DC bias is removed, oxygen permeates out of the cavity leading to a decay of the Nernst potential. Electronic conductivity of YSZ corresponding to the ambient oxygen pressure is determined by analyzing the decay of the Nernst potential. The measured electronic conductivity is in good agreement with literature values. A manuscript based on this work was published in the *Journal of Power Sources* (2016).
- A YSZ tube with Pt electrodes was used for the measurement of potential with one electrode exposed to air and the other to  $\text{H}_2\text{-H}_2\text{O}$  gas mixtures. Measurements were conducted over a temperature range from  $30^{\circ}\text{C}$  to  $475^{\circ}\text{C}$  using two different meters, one with an input impedance of 10 G  and the other voltage of 0.93 V was measured at  $30^{\circ}\text{C}$ , while it was much lower with the low impedance meter. From the measurements, the actual cell voltage and the net cell resistance including all polarization resistances were estimated. Above  $275^{\circ}\text{C}$ , the measured voltage was in agreement with the expected Nernst voltage. At lower temperatures, the voltage even with the electrometer was lower than the calculated Nernst voltage indicating that  $\text{H}_2\text{-H}_2\text{O}$  gas phase mixture did not reach equilibrium. Electrochemical impedance spectra (EIS) were obtained. From the EIS spectra, the ohmic resistance was obtained. Above  $75^{\circ}\text{C}$  much of the cell resistance is attributed to electrode polarization. A manuscript based on this work was published in the *Journal of The Electrochemical Society* (2016).
- Disc-shaped samples of 8 mol% YSZ with two embedded Pt + YSZ circular electrodes and contacting Pt wires were made by sintering in air at  $1500^{\circ}\text{C}$ . In one sample, four Pt probes were embedded for local electric potential measurements. Porous surface Pt electrodes were applied

on the two exposed surfaces. The samples were heated in air over a temperature range from 800°C to 900°C. A DC voltage between 1 V and 1.7 V was applied across the surface electrodes and the embedded electrodes, with the positive connected to the surface electrodes. This resulted in the formation of black zirconia between the two embedded electrodes by electrochemical pumping out oxygen. In the sample with embedded Pt probes, the local potential was measured as a function of time. A manuscript based on this work has been published in the *Journal of the Electrochemical Society* (2016).