Materials in Nonequilibrium Thermodynamic States
– on the oxygen electrodes in energy technologies

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Much of our understanding of physical behavior of materials is based on the concept of equilibrium, which lies at the heart of classical thermodynamics, condensed matter physics, and modern reaction kinetics. If a thermodynamic system is in equilibrium conditions, which is the situation when an energy system (e.g. a fuel cell or a battery) is under open circuit voltage, the surface and bulk of the electrode are only subject to fluctuation of thermodynamic qualities (e.g. temperature: T, pressure: P, molar number: n, and the chemical potential: μ). For the cases that are not at equilibrium, but are close to it, Onsager established linear reciprocal relationships between flux and thermodynamic force for a thermodynamic system in nonequilibrium states. These linear relationships are manifested in transport phenomena, which are nonequilibrium processes, such as ion diffusion and heat conduction.

However, if an electrochemical reaction takes place at the electrode of a fuel cell or battery, the thermodynamic system is in nonequilibrium nonlinear regime. An electrochemical reaction involves the transfer of matter and energy across the surfaces, which does interact with the exterior; therefore the thermodynamic states of the bulk of the materials are subject to external thermodynamic forces (e.g. ΔT, Δn or $\Delta\mu$). As a result, in an active electrode, the electrochemical reaction on the surface causes all thermodynamic variables to change in both the surface and the bulk.

In this seminar, I will briefly describe material physics and solid-state electrochemistry in four research areas that are being pursued in my group: (1) high rate electrodes in lithium-ion batteries for transportation use, (2) the electrocatalysts for carbon dioxide reduction, (3) thermoelectric oxides, and (4) defect chemistry.

I will use the oxygen electrode in fuel cells and lithium-air batteries as an example to address three questions related to materials in nonequilibrium thermodynamic states: (i) how do fast kinetics and high current in an operating fuel cell affect the thermodynamic states of its material constituents, (ii) whether or not the state of nonequilibrium can remain stable with constant flow of matter and energy, and (iii) what are the electrode materials that can be designed from theoretical studies?