A holistic approach to understanding batteries and fuel cells: combining impedance spectroscopy with multiscale materials simulation.

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Collaborator: Stephen Skinner (Materials, Imperial College London)

Abstract
Peeking inside opaque matter is a trick used at airport security checks. Impedance spectroscopy [1] is a handy method that allows us to look inside fuel cells and batteries, by applying an oscillating voltage \( V(\omega) \), across a sample, measuring the current response, \( I(\omega) \), and calculating the complex impedance, \( Z(\omega) = V(\omega)/I(\omega) \). In principle, the impedance contains information about every electrochemical and diffusive process occurring within the sample on the time scale \( \sim 1/\omega \) of the applied voltage. The goal of this project is to use multi-scale materials simulations to decipher this information and to understand better the inner workings of batteries.

An impedance spectrum is usually interpreted, first, by finding an effective linear circuit composed of resistors, capacitors and inductors, that reproduces the spectrum; next, the inner workings of the device are inferred by identifying individual effective-circuit elements with processes in the material (resistance with bulk diffusion, capacitance with interfacial layers, etc). This approach relies on key processes being guessed/deduced correctly, and on their coupling, being sufficiently simple or weak that they can cleanly be identified (individually, or in combination) as contributing a simple component to the effective-circuit. This can often be very difficult and more input from theory and simulation is badly needed.

We will simulate a complete device using continuum models of coupled “reaction-diffusion” processes [2,3], seeking consistency between theory, simulation, and the measured spectra. Novel open-boundary atomistic simulations will be used to elucidate fundamental steps in the reaction and diffusion processes and to calculate their rates [4]. We will start with a well characterized system (Pt/YSZ/Pt cell) to verify the robustness of the methods, and then use them to study and improve Mg based metal-air batteries.

This is an interface project that involves collaboration with experimentalists from the CDT in Advanced Materials Characterisation: In-operando evaluation of interfaces in solid state electrochemical devices.


An overview of reaction-diffusion systems, with a list of useful references, can be found at http://www.scholarpedia.org/article/Reaction-diffusion_systems
What is the multi-scale nature of the project?
A battery has macroscopic dimensions and functions via numerous coupled processes, involving chemical reactions and/or diffusion of ions and electrons, and having a wide range of characteristic time and length scales. An inefficiency of any one of these processes has the potential to make it the bottleneck that limits the battery’s performance.

In this project, we will consider the performance of a battery as a whole, invoking thermodynamics to integrate out unnecessary detail (e.g. heterogeneity in planes normal to ion transport), and coupling processes with widely differing time and length scales. We will use coupled reaction-diffusion equations for continuum modelling and ‘zoom in’ on key reactions or diffusion mechanisms that deserve in-depth study with electronic structure methods.

How do the expertises of the supervisors complement each other?
Paul Tangney has wide experience of the simulation of materials, and will bring his expertise in solving coupled reaction-diffusion equations to the project.

Andrew Horsfield developed the implementation of Hairy Probes in Plato, and is an expert in Tight Binding (an efficient simplified electronic structure method suitable for demanding atomistic materials simulations).

The experimental collaborator is Stephen Skinner who is an expert in fuel cells and batteries, and who will oversee the experimental project aligned with this project.

Literature Review
What impedance spectroscopy can tell us about the inner workings of a battery - in principle and in current practice.


MSc Project
During the MSc project, a simple 1-D code will be written to solve a set of coupled reaction-diffusion differential equations for the Pt/YSZ/Pt system, with an applied bias. One aim will be to get a feel for the wonderful richness and complexity of even simple reaction-diffusion systems. For example, in 2-D or 3-D “Turing patterns” (e.g. a zebra’s stripes) can emerge from a remarkably simple coupled set of physical processes [1]. Another aim will be to understand the considerable numerical difficulties associated with solving “stiff” equations on a computer. The primary objective will be to clearly and consistently identify reaction-diffusion processes in this system of electrodes and electrolyte, with features of its impedance spectrum.