Understanding the mechanism of Li-O₂ battery via quinone mediators

The non-aqueous Li-O₂ battery [1] is considered the ultimate battery as it possesses 10 times higher theoretical energy density than the state-of-the-art lithium ion battery. The discharge typically involves O₂ reduction in two steps: i) one electron electrochemical step to form LiO₂, which chemically disproportionates to form Li₂O₂ and ii) a solid phase precipitates out of the liquid electrolyte that deposits on the porous electrode.

We would like to study the reactions that occur in a battery by using quinones as redox mediators for the oxygen reduction reaction (ORR) in Li-O₂ batteries. Quinones are an important class of organic redox molecules that are involved in energy transduction and storage in biological systems. The unique charge transfer capabilities of this class of molecules are the reason why researchers are studying their applications for artificial energy harvesting and storage devices.

This project involves density functional theory (DFT) calculations in combination with existing experimental data [2] to gain understanding on fundamental level of the processes that take place in a Li-O₂ battery. During the project, students will learn and become proficient with Linux, VIM, high-level DFT codes. No previous computational experience is required. Successful applicants will be ambitious, passionate, self-motivated, hard-working, and creative students. Further details may be obtained by contacting Prof. Clare Grey.

**From MOFs to frustrated magnetic lattices**

Metal-organic frameworks, made up of metal atoms or clusters linked by organic ligands, can adopt huge range of different structures, and have the potential to exhibit unusual magnetic order, such as spin liquid states. The structures of MOFs can be conceptually represented as a topological network of nodes and linkers, but it is not known which topologies are able to show these unusual properties. In this project you would use computer simulations, including classical monte carlo and mean field methods, to classify network topologies by their magnetic order, and hence identify new materials that could show these weird magnetic behaviours.

**In Situ Study of Quinone-based Redox Flow Batteries by NMR/MRI Techniques**

Electrolyte degradation, diffusion, crossover and distribution will be measured by NMR/MRI techniques in home-built in situ redox flow cells. The student will learn to perform Nuclear Magnetic Resonance (NMR) spectroscopy, Magnetic Resonance Imaging (MRI), Pulse Field Gradient (PFG) diffusion measurement as well as the redox chemistry of quinones.

**Interfaces in lithium-ion solid state batteries**

The main goals for attractive energy storage systems are safety, reliability, and resource/cost efficiency. Lithium ion batteries (LIBs) are one of the most promising storage systems due to their high energy densities and voltages. However, most commercial LIBs are based on organic (liquid) electrolytes that are usually flammable and often toxic. A malfunctioning or damaged battery bears the risk of thermal runaway and subsequent explosion. Therefore, a transition towards safe and reliable solid electrolytes (SEs) would be extremely beneficial.

Despite the fact that all-solid-state batteries are a promising alternative to classic LIBs, only little is known on the exact nature and behaviour of the interfaces that are produced during synthesis and how these interfacial structures change during operation in all solid-state batteries. This project focuses on the study of composite anodes and cathodes consisting of the active material (AM) mixed with a SE and conductive carbon (Figure 1). The student will learn to use classic solid-state synthesis routes (ball milling, annealing) to produce the materials and control their particle sizes. SPS (Figure 2), a novel processing technique, will then be applied to produce dense composite pellets.

In the end, the student will study the materials with XRD to determine phase purity and changes to the pristine state, solid state NMR to gain insights into different chemical environments on the local scale of NMR as well as cycling of the electrodes in a battery to understand the electrochemical behaviour of the materials.

**Figure 1.** Schematic diagram of a cathode mixture with active material (AM), solid electrolyte (SE), and carbon (C).

**Figure 2.** Schematic diagram of an experimental setup for spark plasma sintering (SPS).
Understanding the interfacial stability of Si anode in lithium ion batteries

Forming an interfacial passivation layer on Si is important to achieve long term cycling. Conformal coating Si with polyacrylonitrile with subsequent pyrolysis has yield impressive electrochemical performance, which has been reported by several independent groups. [1-3] Han et al. [3] coated meso-porous Si MP with PAN, which was subsequently pyrolysis at 700˚C to form a carbon coating Si, potentially with Si-N-C bond (Figure 1). The authors demonstrated a Si half-cell with 100% capacity retention (~400mAh/g) after 2000 cycles. The interfacial structure between the coating layer and Si surface may be the key factor for electrochemical enhancement. However, such interfacial species is difficult to characterize by XPS, and TEM. Here, we want to gain a more detailed understanding of such interfacial species by $^{29}$Si DNP NMR.

We will first systematically investigate the coating parameters (e.g. PAN/Si mass ratio; pyrolysis temperature, cell fabrication parameters etc.) Then, we will correlate these factors to their electrochemical performance. Finally, we will try to understand how the Si surface species evolve as a function of cycling using ssNMR and DNP NMR.

Figure 1. Possible reaction mechanism of heating PAN to 700˚C and forming the Si-N-C layer. Taken from Ref 3.