The Grey group tackles a broad range of materials science and energy storage challenges that include various aspects of solid state chemistry, spectroscopy, and theoretical studies. To understand and control the materials that are desirable for energy storage applications, we use a suite of synthetic and analytical techniques, including diffraction, microscopy, solid state NMR, and computation. There are several Part III projects available that contain both experimental and computational aspects. A selection of potential projects is listed below. In addition, students are welcome to propose research projects in adjacent fields.

**Metal-Organic Frameworks**

*Functional hybrid organic-inorganic materials*

Dense hybrid organic-inorganic frameworks are an extremely exciting class of materials, with spanning the alkyl ammonium lead halide solar cell materials and multiferroic formate perovskite frameworks. Work in the Grey group has shown that by using new molecular ligands (such as thiocyanate) we can make new materials with a wide range of interesting properties, including quantum spin liquids, hosts for reversible lithium intercalation and strongly light-absorbing materials. In this project you would synthesise new examples of these frameworks, and then characterise them, with a particular focus on understanding the electronic, magnetic and electrochemical properties of these materials. This is an experimental project, and so in addition to synthesising these materials, you would also make extensive use of X-ray diffraction (both powder and, where appropriate, single crystal), SQUID magnetometry and spectroscopic measurements.
**Battery Materials**

**Novel -CN- based materials for Energy Storage**

Na-ion batteries (NIBs) hold promise to become the main energy storage technology for the grid (Figure 1), replacing toxic Pb-acid batteries and more costly lithium ion batteries (LIBs), despite recent cost reduction. While initial Na-ion cells are based on material analogues to those of Li-ion chemistries, unexplored -CN containing materials hold promise for their performance in both rechargeable battery chemistries.\(^1\) Based on the previous performance shown by polymeric Schiff bases,\(^2\) the goal now is to explore hierarchically ordered Schiff bases or Covalent Organic Frameworks (COFs) for their performance in Na-ion batteries.

This project will involve several mild temperature organic/inorganic synthesis routes as well as solid state characterization techniques such as powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and spectroscopic techniques such as infrared (IR) and Raman. The influence of the chemical composition, and pore size on the structure and on the electrochemical performance for rechargeable Li-ion and Na-ion batteries will be studied.

![Figure 1. Next generation Na-ion batteries store electrical energy from renewables to power the grid.](image)

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**MAX and MXene Chemistry: A Novel Class of Two–Dimensional Li-ion Battery Materials**

Transition metal carbides and nitrides, entitled “MXenes”, are an exciting new class of two–dimensional materials that possess interesting properties for applications such as high–rate Li–ion batteries.\(^3\) MXenes are 2D crystals derived from MAX phases where M is a transition metal, A is usually Al, and X is carbon or nitrogen. In a previous Part III project from our group, we used solid state nuclear magnetic resonance (NMR) to probe the surface chemistry of a titanium carbide MXene.\(^4\) Applications of MXenes as batteries and supercapacitors are emerging but fundamental studies are required to understand the mechanisms and local structure.\(^5\) This project will employ electrochemical techniques and solid state NMR as tools to investigate the nature of this family of compounds and their behaviour upon lithium insertion.

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Battery Materials for All-Solid State Batteries

The main goals for attractive energy storage systems are safety, reliability, and resource/cost efficiency. 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. In addition, Na-ion batteries are a promising alternative for long-term energy storage sustainability in terms of both cost and natural abundance. Despite the widespread hypothesis that SEs would deter the formation of dangerous metallic microstructures (e.g. dendrites) during electrochemical cycling that lead to short-circuiting and catastrophic cell failure, the formation of Na dendrites in the Na superionic conductor (NASICON)-type solid electrolytes (e.g. Na$_{1+3}$Zr$_2$(P$_{1-x}$Si$_x$O$_4$)$_3$) has been reported.$^6$

Sophisticated synthesis and diffusion studies of the solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)

While anode and cathode materials of LIBs are relatively well studied, SEs with high ionic conductivity and stability are rare. The most promising SE is LLZO, which is the only stable candidate towards the ideal anode material, metallic Li. However, Li dendrite formation and potential polarization at interfaces of the electrolyte are unresolved issues. In this project, the student will synthesise large LLZO single crystals by high temperature flux methods in order to compare them to micro-crystalline powder samples (prepared by ball milling and annealing) to study dendrite formation and diffusion. In addition, synthesis of $^6$Li enriched LLZO as well as electrochemical cycling of regular LLZO with a $^6$Li metal anode will allow in situ solid state NMR experiments to study the behaviour at the interfaces and diffusion coefficients when applying different voltages (AC and DC). XRD will be used to check phase purity and the orientation of the single crystals of LLZO.

Monitoring Na dendrite growth in solid electrolytes in real time

Currently, factors such as Na penetration through grain boundaries, large volume changes in the electrolyte, and instabilities in the solid-solid electrode-electrolyte interface are believed to contribute to Na dendrite growth in SEs. Unfortunately, many of these parameters are difficult to investigate with traditional materials characterization strategies because they involve non-crystalline phases transformations and continuously change during electrochemical cycling, requiring monitoring in real time. To bridge this characterisation gap, this project will focus on using in situ $^{23}$Na NMR spectroscopy and magnetic resonance imaging (MRI) techniques to monitor Na dendrite growth in NASICON type materials as the cell is (dis)charged. In this project, SE pellets of Na$_3$Zr$_2$PO$_4$(SiO$_4$)$_2$ will be prepared by spark-plasma sintering (SPS) and characterized by XRD and solid state NMR spectroscopy. Ultimately, the student will be able to correlate what conditions lead to Na dendrite growth in NASICON materials and come up with possible strategies to mitigate microstructural growth and explore these hypotheses.

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

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. The student will learn to use classic solid state synthesis routes (ball milling, annealing) to produce the materials and control their particle sizes. SPS, 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 impedance spectroscopy (EIS) and cycling of the electrodes in a battery to understand the electrochemical behaviour of the materials.

![Figure 2. Schematic diagram of a cathode mixture with active material (AM), solid electrolyte (SE), and carbon (C).](image)

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

Despite the fact that Na shows many similar characteristics to Li, significant differences are observed in their electrochemical behaviour (e.g. graphite is unusable as Na anode). Therefore, the knowledge on interfaces in all-solid state Na batteries is scarce even compared to their Li counterparts.

In this project, the student will synthesize SEs and different AMs, which will then be combined into composite electrodes using SPS. In addition to the techniques used to study Li solid state batteries (e.g. XRD, NMR), electron dispersive X-ray spectroscopy (EDX) will allow a quantification of the local elemental composition, most importantly of Na. This is a great advantage, since Li is invisible to EDX. EIS and cycling of the electrodes in a battery will be used as well.

![Figure 3. Schematic diagram of an experimental setup for spark plasma sintering (SPS).](image)
Solid state ionic conductivity

$^1$H, $^2$H Variable Temperature Solid-State NMR Studies of H-conducting BaH$_{2-x}$

The development of a purely hydride anion (H$^-$) conducting material has been called a "last frontier" in solid state ionics, but has recently been achieved in the alkaline-earth metal hydrides. Notably, the BaH$_{2-x}$ system displays impressively high ionic conductivity, 0.2 S cm$^{-1}$ at 630°C, that is an order of magnitude larger than the best protonic and oxide-ionic conductors. Verbraeken et al. have suggested the marked increase in ionic conductivity of BaH$_2$ near 500°C arises from a first-order transition to a layered hexagonal phase (Figure 1); however, mechanism details of the H-conductivity remain unknown. It is moreover unclear why CaH$_2$ and SrH$_2$ do not exhibit comparable H-conductivity. In principle, $^1$H and $^2$H solid-state NMR spectroscopy can report on ion dynamics in metal hydrides, but has not yet been applied to pure H$^-$ conductors. In this project, we will synthesise BaH$_2$ (BaD$_2$), SrH$_2$ (SrD$_2$), and CaH$_2$ (CaD$_2$), and perform $^1$H and $^2$H solid-state NMR experiments up to 750°C with a laser-heated NMR probe to investigate the phase transitions and H-conductivity. Variable temperature relaxometry experiments, i.e., measurements of longitudinal ($T_1$) and transverse ($T_2$) relaxation times, will also be carried out to extract hydride motional rates and activation energies for H-conductivity. Finally, $^{135/137}$Ba, $^{83}$Sr, and $^{43}$Ca solid-state NMR spectra will be acquired to follow changes in the cationic framework.

Figure 4. The high-temperature, H-conducting hexagonal polymorph of BaD$_2$, resolved by neutron diffraction; the D1 sites are actually split into two partially occupied, disordered environments (not depicted) which suggests their involvement in the ionic conductivity mechanism.

A combined DFT and experimental study of the structure, stability, and selected physical properties of ceria slab crystal structures

The ceria (CeO$_2$) structure is important in materials science, as it has a high oxygen ion conductivity due to the Ce$^{4+}$/Ce$^{3+}$ redox couple presence. However, pure CeO$_2$ is not able to reduce and oxidize efficiently over many cycles, so transition metals are incorporated to overcome this shortcoming. Adding transition metals helps stabilize the ion conductivity of ceria, as often the properties of such material depend strongly on the defects and distortions. One of the promising transition metals able to enhance the catalytic activity of ceria is copper, so the ability of copper to control the composition, structure, and properties will be studied in this project.

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$^7$ Yamaguchi, S. Science 2016, 351 (6279), 1262–1263.
This project involves a combined theoretical density functional theory (DFT) and experimental study of Cu defects in a series of CeO$_2$ slab models (mainly low index surfaces (111), (010), and (001)), where students will learn and become proficient with Linux, VIM, high-level DFT codes, as well as materials preparation and characterization. No previous computational experience is required. Successful applicants will be ambitious, passionate, self-motivated, hard-working, and creative students.

**Melamine and melem based g-C$_3$N$_4$ - a combined DFT and experimental study**

The development of new efficient and cheap photocatalysts for water splitting is essential for industry, and therefore, g-C$_3$N$_4$ has become a new research hotspot and drawn broad interdisciplinary attention as a potential metal-free photocatalyst. Despite the high interest among the scientific community, the exact structure of these 2D materials is still not fully understood, and the synthesis of pure g-C$_3$N$_4$ remains a challenge. The focus of the project will be to obtain fundamental understanding of the structure, stability, and selected physical properties of these semiconductors. This will be accomplished by examining different model stacking arrangements in melamine and melem based materials.

This project involves a combined theoretical density functional theory (DFT) and experimental study of g-C$_3$N$_4$ in series of AB stacking models, where students will learn and become proficient with Linux, VIM, high-level DFT codes, as well as materials preparation and characterization mainly via X-ray powder diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy. No previous computational experience is required. Successful applicants will be ambitious, passionate, self-motivated, hard-working, and creative students.
Carbon Capture

Development and in situ studies of novel ceramics for CO$_2$ capture and looping

Coal fuels more than 40% of global electricity production, and is responsible for over 40% of global CO$_2$ emissions. Further, coal is widely distributed across the Earth, and demand continues to grow. While we continue to develop alternative and renewable power sources, the capture and sequestration of CO$_2$ from flue gas in fossil fuel power plants and other industrial processes is one viable solution to decrease our CO$_2$ emissions. CO$_2$ can be removed from flue gas by chemical looping, where a material chemically reacts with CO$_2$ and is treated at a later stage to release pure CO$_2$ and regenerate the starting material. Limestone, CaCO$_3$, is the oldest material to be used for this purpose. However, although limestone is abundant and cheap, the CO$_2$ absorption capacity rapidly decays with use because of undesirable changes to the microstructure.

They Grey Group is developing novel CO$_2$ looping materials that can be cycled hundreds of times without loss in performance, and is investigating materials that demonstrate surprising performance near room temperature, compared to most materials that operate at several hundred degrees Celsius. The part III student for this project will explore new ceramic chemical looping materials, and will prepare and characterize them using bespoke instrumentation already designed and built for this experiment.

The student will be guided by post-doctoral scholars and be part of an active research community, and will learn important material preparation and characterization techniques during their tenure. Some techniques will include XRD, thermal gravimetric analysis, microscopy, and spectroscopy (NMR, XPS, XANES, EXAFS). At the end of this project, the student will have working skills to prepare ceramics, determine the atomic structure and composition, determine the CO$_2$ sorption properties of materials, and contribute towards a socially and environmentally conscious research project. Successful applicants will be ambitious, passionate, self-motivated, hard-working, and creative students.