**University of Leicester**

**Chemistry GTA Studentship Project 2022**

**Section 1 – *Supervisor Information***

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| **First Supervisor (Name and Title)** | Prof Robert Hillman |
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**Section 2 – *Project Information***

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| **Project Title** | Stress, Morphology and Material Properties of Electrodeposited Aluminium in Novel High Energy Density Battery Systems | |
| **Project Highlights:** | 1. | Dynamic real-time determination of stress in depositing Al films |
| 2. | Identification of conditions (electrolyte, temperature, voltage) yielding stress-free Al films |
| 3. | Correlation of Al film stress characteristics with spatially resolved structure from CT measurements |
| **Project Overview** | | |
| Rechargeable battery systems for stationary energy storage, mobile electronics and electric vehicles are dominated by lithium-based technologies. However, aspects of their safety, materials availability (limited by abundance, strategic factors or conflict zone origins) and performance are less than ideal. This motivates development of other technologies. Amongst these, aluminium (Al) based batteries are of particular interest based on global resource availability, cost, density and – not least – the fact that a *trivalent* ion (cf. *monovalent* lithium) potentially offers three times the energy.  There are two aspects to the underlying Al chemistry, associated with solution and interfacial phenomena. The former encompasses speciation (metal ion complexation) and transport dynamics (to the electrode); we have recently addressed these for some novel aluminium-based electrolytes (see below). The latter centres on the electrodeposition of the elemental aluminium via a sequence of nucleation and growth processes: these and their consequences are the focus of this project.  The vision is an integrated composition-structure-dynamics-characteristics picture of electrodepositing and dissolving Al layers, as the electrode undergoes a charge-discharge cycle. The process will be driven electrochemically by the application of a potential control function. Various waveforms will be utilised to temporally manipulate and resolve nucleation and growth steps and rates; avoidance of dendrite formation – a cause of failure and fire in lithium batteries – and delamination are crucial targets. Composition issues involve electrolyte occlusion, which can be profiled vertically using time-resolved neutron reflectivity (see below) and mapped in 3D using CT (via our Faraday Institution collaborations). Stress phenomena – the primary novelty of the project – will be determined using a sophisticated variant of the quartz crystal microbalance (QCM); see methodology. Assembly of these components for a range of electrolytes and substrates will provide an unprecedented level of detail for future Al battery system design.  The student will gain experience of diverse materials and battery science presently in high demand (inter)nationally in both academic and industrial institutions. This will be facilitated through the Materials Centre (Leicester), large neutron and X-ray facilities (ISIS, ILL, Diamond), and the Faraday Institution (<https://www.faraday.ac.uk/>). | | |
| **Methodology** | | |
| Electrochemistry defines the chemical environment, through control (potential) and measurement (current) of interfacial processes. Mechanistic diagnosis of responses will distinguish instantaneous *vs* progressive nucleation, identify growth dimensionality, and identify and quantify the rate limiting process (interfacial reaction *vs* solution transport).  The technical and intellectual core of the project is determination, rationalisation and ultimately removal of mechanical stress effects in the electrodeposited Al films. This will be accomplished using the *double resonator* QCM technique, a sophisticated variant of this acoustic wave technique exploiting the distinct gravimetric and stress response components of AT- and BT-cut quartz resonators. While an established technique, very few QCM publications (< 0.01%) exploit the double resonator capability; there is substantive novelty here. We will explore time domain effects via higher harmonic measurements and temperature variation (analogous to time-temperature correlations for polymer films).  Film characterisation by neutron reflectivity (NR) and surface imaging (3D microscopy, AFM, SEM/EDX, CT) and electrolyte speciation (XAS) will provide supporting structural rationalisation. Assembly of these elements for a range of electrolytes and substrates will provide an unprecedented level of detail for future Al battery system design. | | |