Engineering and Innovation Research Studentship 2023/2024

Project title:	**Advanced Functional Materials as Electrodes in Water-in-Salt Electrolytes (WISE) for Aqueous Rechargeable Batteries**
Discipline	Materials Engineering, materials for energy, Electrochemical Energy storage
Key words:	2D materials, water-in-salt electrolytes, aqueous rechargeable batteries
Supervisory team:	Satheesh Krishnamurthy, Zahra Golrokhi, Nicholas Power
URL for lead supervisor's OU profile	http://www.open.ac.uk/people/sk9268

Project Highlights:

- Development of advanced 2D materials for high energy density aqueous rechargeable batteries in water-in-salt electrolytes.
- "Water-in-salt" electrolytes significantly extend the electrochemical stability window to 3 or 4 volts, leading to a new series of high-voltage aqueous metal ion chemistries.
- Demonstration of proof-of-the-concept prototype high energy density aqueous batteries.

Overview:

Aqueous secondary batteries have attracted a great deal of attention due to their inherent properties of non-flammability, low cost, and excellent ionic conductivity of aqueous electrolytes. However, the narrow electrochemical stability window (1.23 V) imposed by hydrogen and oxygen evolution limits the overall energy density of the battery. Recently, a new water-based electrolyte, salt-in-water (WiS) electrolyte, has extended the electrochemical stability window of water-based electrolytes to about 3.0 or 4.0 V. This is because the average number of water molecules in each ionic solvation structure is much lower than that of the ionic solvation structures in normal dilute solution electrolytes. The ionic solvation structure and bulk structure of the electrolyte changed significantly, which changed the interfacial chemical reaction of the electrolyte at the electrode surface, thereby widening the stable electrochemical window of the aqueous electrolyte. This leads to a new set of aqueous high voltage metal ion chemistries.

Two-dimensional (2D) materials are commonly used to design electrodes for aqueous batteries due to their typically large surface area, large number of ion transport channels, and large number of active sites. It also acts as an anode/cathode active material and conductive additive in secondary batteries. The main focus of research is on monovalent (Li^+, Na^+, K^+, H^+) and multivalent (Mg^{+2}, Zn^{+2}, Al^{+3}) ions.

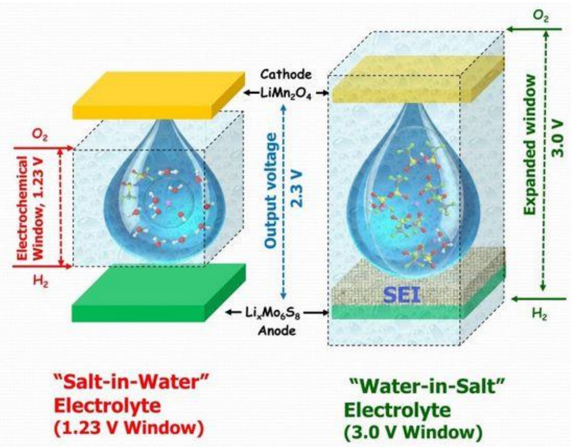

Figure 1. Full aqueous Li-ion battery using a model electrochemical couple (LiMn2O4 and Mo6S8) and demonstrated an open circuit voltage (OCV) of 2.3 V. [Science 350 (6263), 938-943]].

Methodology:

The aim is to synthesize and surface engineer (or doping) a variety of 2D materials (based on oxides/carbides/sulfides/nitrides, and Mxene). The obtained 2D materials are further characterized by physical and electrochemical techniques according to our proposed work. Detailed studies of reaction mechanisms are performed using a variety of in situ/operando and ex-situ spectroscopic tools. The ultimate goal is to produce a proof-of-concept and prototype of a high-energy density aqueous battery. This is achieved by a pair of developed 2D materials with a suitable cathode (commercially available) in water in salt electrolyte.

Physical characterisation:

Physical characterizations such as XRD, SEM/TEM, N2 adsorption/desorption, Raman, XPS, and ICP are performed inhouse for phase purity, morphology, surface area, and electronic properties to optimise the right structure. As charge transfer/chemical bonding plays a key role in band gap engineering of these 2D materials: fundamental information that are key to device fabrication.

Electrochemical Characterisations:
The kinematic studies of these materials and interfaces will be carried out using autolab. The electrodes will be applied to current collectors (glassy carbon, stainless steel, Ti, etc.) and dried under vacuum. The electrodes will be mounted in two-electrode and three-electrode cells set up for electrochemical characterization of water in salt. Cyclic voltammetry, galvanostatic cycling, impedance spectroscopy, GITT, PITT will be performed using an electrochemical workstation.

Indication of project timeline:

Year 1: Literature survey and selection of the materials synthesis and optimisation.

Year 2: Electrochemical characterizations/ surface engineering of 2D systems in water in salt electrolytes towards the development of aqueous batteries.

Year 3: Proof-of-the-concept and prototype development of high energy density aqueous batteries, dissemination manuscript writing, Complete thesis write-up.

References & Further reading:

1. Roadmap for advanced aqueous batteries: From design of materials to applications, D. Chao, W. Zhou, F. Xie, C. Ye, H. Li, M. Jaroniec, S. -Z. Qia, Sci. Adv. 2020; 6 : eaba4098
2. Recent advances in “water in salt” electrolytes for aqueous rechargeable monovalent-ion (Li+, Na+, K+) batteries, H. Gao, K. Tanga J. Xiao, X. Guo , W. Chen, H. Liu, G. Wang, J. Energy Chemistry, 69, 2022, 84-99.
3. Novel Hydrothermal Synthesis of CoS2/MWCNT Nanohybrid Electrode for Supercapacitor: A Systematic Investigation on the Influence of MWCNT, A. Sarkar, Amit K. Chakraborty, S. Bera, and S. Krishnamurthy, J. Phys. Chem. C 2018, 122, 32, 18237–18246.
4. Surface Functionalized MXenes for Wastewater Treatment—A Comprehensive Review, S. Krishnamurthy, et al., Global Challenges2022, 6, 2100120.
5. MXene conductive binder for improving performance of sodium-ion anodes in water-in-salt electrolyte, F. Malchik, N. Shpigel, M. D Levi, T. R. Penki, B. Gavriel, G. Bergman, M. Turgeman, D. Aurbach, Y. Gogotsi, Nano Energy, 79, 2021, 105433.
6. Continuous Hydrothermal Synthesis of Metal Germanates (M2GeO4; M = Co, Mn, Zn) for High-Capacity Negative Electrodes in Li-Ion Batteries, D. Bauer, T.E Ashton, A.R Groves, A. Dey, S. Krishnamurthy, N. Matsumi, J.A Darr, Energy Technology, 2020, 1900692

Further details:

Students should have (or expect to obtain) at least the equivalent of a UK upper second-class honours degree (and preferably a Masters’s degree) in chemistry, materials science, solid-state physics/chemistry or other relevant scientific disciplines. Knowledge of synthetic and characterisation techniques for inorganic materials and a broad interest in sustainable chemistry would be an advantage. The student will join a well-established team researching on materials functionalisation for solar energy, solar fuels and electrochemical energy storage group.

Please contact Satheesh Krishnamurthy Satheesh.krishnamurthy@open.ac.uk for further information,
https://satheeshkrishnamur.wixsite.com/nanoenergy

Applications should include:

- A 1000 word cover letter outlining why the project is of interest to you and how your skills match those required
- an academic CV containing contact details of three academic references
- an Open University application form, downloadable from: http://www.open.ac.uk/postgraduate/research-degrees/how-to-apply/mphil-and-phd-application-process
- IELTS test scores where English is an additional language

Applications should be sent to
STEM-EI-PhD@open.ac.uk by 15.02.2023