





Book of Abstracts

2025 Satellite Early Career Researcher Regional Symposium on Electrochemistry (SERRS)

TSI Building Room TSI039

Thursday 30th January 2025



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Keynote Speaker

Frontier Chemistries for Li-ion and K-ion Batteries comprising nanostructured alloying anodes and 3D current collectors

Kevin M. Ryan, University of Limerick

Abstract

I will discuss the performance gains attained in lithium ion and potassium ion batteries when alloying anodes in nanostructured form are used. I will discuss our developments on the synthesis of silicon and germanium nanowires directly from current collectors in a solvent vapor growth system. The versatility of the approach allows high yield synthesis and additionally allows for hybrid compositions with controlled incorporation of both Si and Ge to optimise capacity and rate capability. The transformation of the wires form discrete structures to a porous network during cycling and its implications on performance will be discussed. In addition, the role of electrolyte additives on the SEI stability of alloying anodes in carbonate based and ionic liquid electrolytes will be evidenced by XPS analysis. I will further discuss the modification of the synthetic protocol for the controlled growth of CuxSiy nanowire arrays which form excellent 3D current collectors. Li-ion battery anodes were obtained using amorphous silicon deposition by PECVD and K-ion batteries were obtained using Sb evaporation on these CuxSiy current collector architectures. The 3D NW array provides a strong anchoring effect for the alloying material, while the spaces between the NWs act as a buffer zone for expansion/contraction during cycling. Finally, I will discuss our coordination activity in the Horizon Europe projects Si-Drive www.sidrive2020.eu and SiGNE www.signehorizon.eu for upscaling Si nanomaterials for Li-ion Batteries. Advancements in sensing performance of enzymatic glucose and lactate biosensors for improved healthcare monitoring

Industrial Speaker

From theory to practice; my career in electrochemistry at Dexcom

Richard Bennett, Senior Process Engineer, Dexcom Ireland, Newford, Athenry, Co. Galway.

Abstract

The purpose of this retrospective is to provide one example of a career path for both emerging and established electrochemists in the field. This presentation will explore how fundamental electrochemistry underpins the operation of Dexcom devices. Diabetes is a life-threatening condition with millions of sufferers worldwide and an ever-growing impact. The discussion will focus on how advancements in this area allow us, as a company, to address critical issues faced by people with diabetes. Enhancements to accuracy, sensitivity and reliability of continuous glucose monitors (CGM) are not possible without a strong fundamental understanding of bioelectrochemistry.

The second part of the presentation will focus on my individual career path, from my first research experience in electrochemistry during my time at the University of Galway to the present day where I work as a senior process engineer for Dexcom. This will be aimed at students and researchers who are open to a career beyond academia.

Advancements in sensing performance of enzymatic glucose and lactate biosensors for improved healthcare monitoring

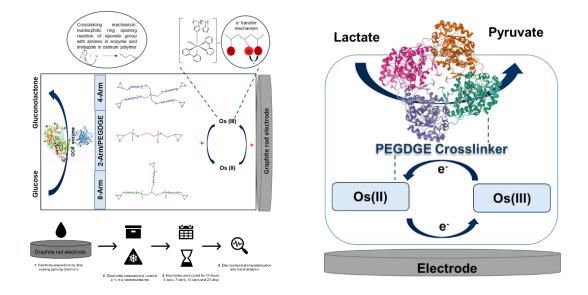
<u>Reshma Kidayaveettil</u>^a, Richard Bennett^b, Andy Mount^b, Dr.Christopher Schulz^c, Dr. Alfons K. G. Felice^c, Prof. Dónal Leech^a

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The increasing prevalence of diabetes and other metabolic disorders necessitates accurate and continuous monitoring of glucose and lactate levels. Electrochemical biosensors provide a potential solution for real-time, point-of-care testing.

Enzymatic electrochemical sensors have emerged as a promising technology for continuous monitoring of analytes due to their high sensitivity, selectivity, and compatibility with point-ofcare applications. The use of osmium redox polymers as mediators has gained significant attention owing to their stability and tunable redox properties^{1,2,3}. A part of this work explores understudied aspects of glucose sensor performance, focusing on the influence of multi-functional epoxide crosslinkers and curing duration in the performance of glucose sensors. The results show improvement in the stability, sensitivity, and selectivity of the sensor, paving the way for advanced point-of-care diagnostics. Another study explores the advantage of using a novel lactate dehydrogenase enzyme as the biorecognition element for sensing lactate in human plasma.

By investigating and optimizing the fundamental aspects of sensing chemistry, this study aims to contribute to the development of more robust and efficient biosensors for both lactate and glucose detection.



Schematic representation of sensing electrode development for glucose and lactate biosensor

01

Enabling early detection of ovarian cancer using a novel electrochemical sensing platform

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Ovarian cancer (OC) is the deadliest gynecological cancer, affecting 300,000 women annually. CA125, the current screening marker, lacks reliability for early detection, missing 20% of cases, and is also known to result in both positive and negative assays. Despite a 90% chance of survival within five years if detected at stage I, only 25% of cases are detected due to inadequate screening methods and initials symptoms. Our research involves the development of a disruptive multiplexed near-patient diagnostic solution, to enable early detection of Stage I and II OC using three different biomarkers.

Gold flexile electrodes were modified with a polymer layer and the antibodies of interest, antiHE4 and anti-CA125, were immobilized on the surface of electrodes. Preliminary results show that the sensor has a linear range of 0.1 fg/ml to 10 pg/ml and 10 fg/ml to 1 ng/ml for HE4 and CA125 respectively. The sensitivity of 0.31 and 0.53 K Ω .mm2 /pg were calculated for HE4 and CA125 in sequence.

This diagnostic device features a new highly sensitive electrochemical sensor that uses multiple biomarkers to achieve greater accuracy.

3D Bioprintable electrically Conductive Bioinks for Biosensing Applications

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3D Bioprinting is emerging as a compelling fabrication technique, facilitating the efficient assembly of intricately designed 3D-printed structures. The appeal lies in the creation of multicomponent bioinks endowed with customized properties, presenting an exciting prospect for driving the rapid expansion of the 3D bioprinting capabilities. This advancement holds the potential to pave the way for the generation of multifunctional tissues, organs, engineered bacterial biofilms, and sophisticated biosensors. Utilizing multicomponent bioactive bioink formulations represents a contemporary and effective approach to improve pre- and postprinting characteristics, encompassing aspects like viscosity, cytocompatibility, bioactivity, and the provision of free-bioactive binding sites within the context of biosensor development. In this context, we introduce an advanced electrically conductive bioink embedded with active biorecognition element for the detection of the target analyte (Streptavidin-biotin). Different conductive fillers were varied and tested to formulate the most suitable bioink for biosensor development. Their incorporation to the polymeric matrix directly effects the rheological, mechanical, biocompatible, and electrically conductive properties of the bioink. Therefore, the effect of these conductive fillers and the corresponding components for a biosensing platform were analysed and studied, e.g., rheological tests, 3D printability and conductivity analysis through cyclic voltammetry and impedimetric approaches.

03

Impedimetric sensing of stimuli-responsive hydrogels for wearable sensors

Rinki Singh, Aoife Morrin

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Interest in wearable bio-diagnostic technologies has grown due to the urgent need for continuous biomarker monitoring. To address this challenge, biosensors need to be integrated with the body using soft, flexible, and often transparent materials that can be designed to respond to specific biomarkers found in skin fluids. Passive sweat as a matrix is particularly promising for non-invasive, continuous biosensing where a key indicator of skin barrier function is sweat pH, which varies under both normal and pathological conditions.

This study investigates a stimuli-responsive polyacrylic acid hydrogel as a skin-compatible sensing interface that can quantitatively respond to physiological changes while ensuring adhesion and flexibility. Hydrogel patches were fabricated, and electrical impedance, a technique suitable for monitoring the bulk electrical properties of hydrogels and compatible with miniaturization and wearability, was employed to characterize hydrogel formulations. The hydrogel's equilibrium swelling capacity was monitored by extracting the bulk gel resistance (R_{gel}) circuit element from the proposed equivalent circuit model. R_{gel} was shown to correlate with water uptake in hydrogels measured gravimetrically. The pH-dependent swelling response was tracked through R_{gel}, maximum ionization of the carboxyl groups at pH 4 resulted in maximum values for R_{gel}.

Formulations were developed to maximise skin adhesion and flexibility, and applied to kiwi fruit tissue for proof of concept as a responsive, adherent wearable material. In-situ measurements of R_{gel} for these wearable hydrogel films demonstrated their sensitivity to changes in surface pH of the kiwi fruit. These findings highlight the potential of soft, responsive hydrogel chemistries for impedimetric tracking of hydrogen ion-induced swelling in response to analyte partitioning from tissue surfaces into the hydrogel, paving the way for the development of wearable biochemical sensing interfaces.

04

Redox-Active Copper Complexes and DNA Interactions: Pathways to Cancer Treatment

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The anticancer ability of copper complexes is attributed not only to their redox activity but also to their interactions with DNA. Copper-based metallodrugs can undergo Fenton-like reactions, generating hydroxyl radical (ROS), which act as potent cytotoxic agents and are valuable in cancer treatment strategies. The DNA damage caused by these radicals can inhibit the proliferation of cancer cells.^[1-3]

Investigations into the *in-situ* formation of copper complexes reveal that they may undergo ligand exchange with anionic species, indicating that their redox activities may be highly complex within biological systems.

To further study radical generation and the interactions between copper complexes and DNA, DNA-modified electrodes were prepared. The DNA-facilitated long-range electron transfer enable the assessment of both the interaction and cleavage efficiency of copper complexes with DNA.^[4–6] This research direction holds promise for elucidating the therapeutic mechanisms and redox chemistry of copper metallodrugs, with the goal of enhancing their efficacy in cancer treatment.

Surface modification of Quartz Nanopipettes for the detection of pathogenic DNA *Klebsiella pneumoniae*.

Shane P. O'Neill, Robert P. Johnson

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Klebsiella pneumoniae is a multidrug-resistant, Gram-negative bacteria ordinarily found in the gastrointestinal tract of humans and also in the wider environment.^[1] Once infected, it is incredibly difficult to treat patients given that the pathogen is now classed as a "superbug" due to its heightened resistance to many antibiotics, notably, carbapenems.^[2] The common mechanism for the increased resistance to drugs is Single Nucleotide Polymorphisms (SNP's).

Nanopores have been used for the detection of many biomolecules and chemical compounds. Recent trends in nanopore sensing brought a prevalence in ion-current rectifying systems in asymmetric nanopipettes, where variations in surface charge affect the current on current-voltage plots, allowing for increased sensitivity.^[3] These systems have been used to detect a variety of compounds including microRNA,^[4] and heavy metal ions such as lanthanum^[5] and mercury.^[6]

Herein, we present a novel system for the modification of quartz nanopipettes for the detection of *K. pneumoniae*. Quartz nanopipettes, were fabricated and modified with DNA complimentary to the *gapA* region of the pathogenic bug, followed by detection of the target sequence. Further, the discrimination of various SNP's was investigated as a function of time to understand the difference in the DNA binding kinetics with regards to the mismatch base pairs. By this, we have developed a modified nanopipette, and an overall framework, which can successfully detect pathogenic DNA through ICR using current-voltage traces.

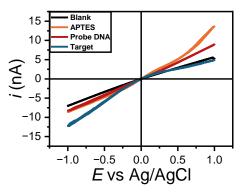


Figure 1: Current Voltage Traces for the unmodified nanopore (black), APTES modified nanopore (orange), probe DNA modified (red) and target detected using the probe modified nanopore (blue).

Multi-parametric electrochemical sensing platform for the detection of pH, temperature, nitrate and nitrate in livestock welfare

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The exponential growth of the dairy sector requires advanced monitoring tools to ensure sustainable practices that benefit the environment, economy, and human health. Current monitoring devices often lack multi-parametric capabilities, limiting their ability to provide comprehensive data on critical chemical and biochemical parameters. To address this challenge, this work presented the development of a real-time multi-parametric device that integrated sensors for pH, temperature, nitrate, and nitrite, providing a holistic approach to dairy cattle health monitoring. This solution included an electrochemical platform, Portable Unit for Lab-on-Site Electrochemistry (PULSE), and an APP for data processing and display. In-house fabricated flexible gold-printed electrodes exhibited a 42.9% increase in the electrochemical active area, when modified with nanoporous gold. These sensors were used for nitrite and nitrate detection achieving limits of detection of 39.27ppm and 20.75ppm, respectively. For pH sensing, a commercial screen-printed electrode coated with a layer of iridium oxide demonstrated a 127.8% enhancement in the electrochemical active area. This system was tested in a real-world scenario, using bovine ruminal complex fluid obtaining a pH sensitivity of -59.63mV/pH and an accuracy of 98.9%. These findings highlighted the potential of this technology as an effective tool for dairy cattle health monitoring and its deployment in real-world scenarios.

One-Dimensional Modeling of Photocurrent Transients: Self-Assembled Porphyrins at the Liquid|Liquid Interfaces

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- 3. Department of Thermodynamics, Faculty of Physics, University of Valencia, Valencia, Spain

Self-assembled porphyrin films have demonstrated high efficiency in facilitating electron transfer across the interface between two immiscible electrolyte solutions (ITIES)[1]. When this film is photoexcited, a coupled set of reactions generates photocurrent responses in transient conditions. The reaction mechanism relies on the presence of an electron donor on the organic side and an electron acceptor on the aqueous side of the liquid|liquid interface[2], [3]. The porphyrin film acts as a bipolar electrode where Faradaic and capacitive processes are involved. We propose a one-dimensional model based on the charge density fluxes to simulate the generation of the photocurrent transient in the presence of neutral electron donor and acceptor species. Our simulations show that the light intensity, as well as the electron transfer, recombination, and product separation constants in the organic phase, significantly influence the magnitude of the initial spike and the decay scope of the dynamic photocurrent transients. Conversely, the aqueous phase's constants do not substantially affect the photocurrent transients in the system helps us enhance the efficiency of the self-assembled porphyrins for their further applications in solar energy and storage devices.

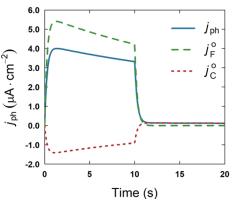


Figure 1. Simulated photocurrent transients' response of the self-assembled porphyrin film at the ITIES. The blue line represents the total photocurrent, while the green and red dotted lines illustrate the Faradaic and the capacitive currents, respectively, in the organic phase of the liquid|liquid system.

Simple and scalable synthesis of iron-nickel-boride trifunctional electrocatalyst for wastewater electrolysis

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Production of energy efficient green hydrogen is key in achieving a vital transition into a carbon neutral economy, addressing climate change. However, to date ultra pure water is used in industrial electrolyzers which is already becoming a scarce resource. In this study, we focused on ammonia rich wastewater electrolysis by developing a trifunctional cost-effective electrocatalyst, with the potential of scalable production. Self-supported iron-nickel-boride electrocatalyst on nickel foam was synthesised through a simple and scalable chemical reduction method. The FeNiB/NF electrodes were tested for their intrinsic catalytic activity and durability for ammonia oxidation reaction (AOR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The bimetallic synergetic effect of iron and nickel combined with the excellent conductivity and porosity of nickel foam, contributed to achieving significant AOR, OER and HER activity. Thus, this work encounters the main challenges regarding green hydrogen production through the development of cost-effective electrocatalyst for wastewater electrolysis.

09

Electrosynthesis of free-standing PEDOT Thin Films using Fe(III) at polarised liquidliquid interfaces

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The electro polymerization of free-standing PEDOT thin films in polarized aqueous|TFT interfaces using Fe(III) oxidants was demonstrated in this work. Modulated polymerization of PEDOT films at polarized liquid|liquid interfaces was recently reported using Ce(IV) as oxidant in acid media1 . The assembly of the oligomers occurs at the interface, generating a floating film which facilitates their extraction and adaptability for multiple post-synthesis applications, in areas as energy harvesting and storage2 , and drug delivery technology3 . Methods such as Closed Bi-Polar Electrochemistry (CBPEC) allowed us to compare the mechanism of Heterogeneous Electronic Transfer (HET) of multiple biphasic systems4 , revealing dependences with the iron coordination sphere, and an estimate potential of at least 0.741 V on the Galvani scale for the electronic transfer at the interface. In parallel, the incorporation of MWCNTs and chemical polarization facilitated charge transfer through the interface during polymer synthesis. Experiments in 4-electrodes cell evidenced the successful formation of the film, regardless of the weak oxidizing power of Fe(III), disclosing a novel interfacial polymerization pathway.

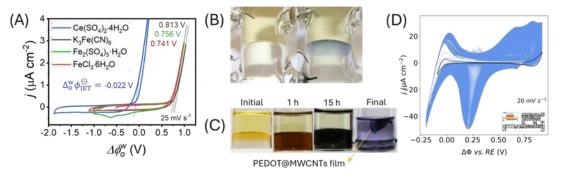


Fig. 1 Interfacial electropolymerization of PEDOT thin films in 4-electrodes cell configurations. A) Onset potential for the HET measured using voltammetry in a CBPEC cell. B) Free-standing PEDOT thin film electropolymerized using Fe(III) as oxidant. C) Synthesis catalysed by MWCNTs and LiTB in an electrodeless cell. D) Successive scans for the interfacial electropolymerization of EDOT at the interface FeCl3, HCl || EDOT, BATB, TFT.

In search of sensitivity for nanoscale sensing systems

Dominik Duleba*, Adria Martínez-Aviño, Robert P. Johnson

School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland Nanopore, nanopipette, sensitivity analysis, optimization, Sobol' method, uncertainty

Nanoscale sensors often operate on physical principles that are highly non-linear and highly coupled. For example, in nanopore sensors, the immobilization of an analyte to the surface alters the surface charge density, which couples into the ion transport, the fluid flow, the electrostatics of the system, and even into the molecular behavior of the surface such as surface protonation and deprotonation. Identifying the conditions where such nanoscale sensors show the highest sensitivity in terms of the statistical discrimination of two different analytes, or the statistical discrimination of a sample from the baseline is not trivial, and would require a high number of experiments where the parameter space is swept, yet the throughput of nanoscale devices is often low. We present the use of finite element analysis together with techniques such as kernel density estimation and SOBOL sensitivity analysis to theoretically explore the parameter space of nanoscale electrochemical sensors. We obtain the expected distribution of output measurements taking into account the random errors associated with sensor fabrication, and obtain heat maps that show when statistical discrimination between the baseline and target measurement is greatest. We also explore how operating the sensor in different regimes (such as low electrolyte concentration vs high electrolyte concentration) can result in the random errors associated with fabrication having a different extent of an influence, which again is related back to the sensor sensitivity. We think our work can help guide the sensor community into understanding and optimizing the sensitivity of their devices with a lessened experimental load.

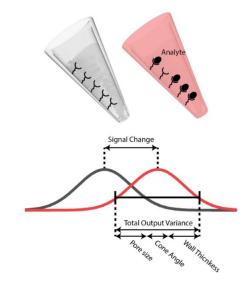


Figure 1 Illustration of the expected baseline and target output distributions of a nanopore sensor highlighting the signal change as well as the main components of the distribution's variance. The goal of the simulations is to make these distributions as distinct as possible.

Trimolybdate substituted Dawson Polyoxometalates doped Poly(3,4ethylenedioxythiophene) films: a volumetric study.

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The successful utilization of POMs requires it to be used continuously for its designed application. However, homogeneous catalysts are less recoverable upon utilization, hence the need to heterogenize the POMs with a substrate. the nature of the substrate for high-performance heterogeneous catalysis requires meeting the following criteria: good stability, porosity, high surface-to-volume ratio, and catalytic activity. Various substrates have been reported in the literature for making POMs composites. These include porous matrices such as activated carbons, conductive polymers, like PEDOT, and layered compounds such as graphene oxide. Combining the properties of the substrate and the POMs gives rise to new and sometimes synergistic characteristics beneficial to sensing and catalysis. Discovering new properties requires investigating POMs when they are combined with other materials. In this work, we report incorporating two POMs namely, $[P_2Mo_3W_{15}O_{59}(H_2O)_3]^{6-}$ and $[P_2Mo_3W_{15}O_{62}]^{6-}$ into the PEDOT. Subsequently, the electrochemistry of the composite is investigated, and the effects of pH and POMs loading in the matrix are examined. Comparing the POMs in PEDOT to its solution electrochemistry revealed that PEDOT increased the POM's stability over a wider pH range. Additionally, Cyclic voltammetry showed effects that were attributed to the interaction of POMs with conductive polymer.

012

Film Formation on electrochemical investigations of NSAIDs such as Diclofenac and Mefenamic Acid.

Kevin J. Kurian, John Cassidy, Anthony Betts

Investigations were conducted into electrochemical behaviour of Diclofenac (DCF) and Mefenamic acid (MFA), two widely used non-steroidal anti-inflammatory drugs (NSAIDs). Their frequent presence in aquatic environments necessitates rapid, cost-effective detection methods, as conventional techniques like mass spectrometry and chromatography are costly and time intensive. During Cyclic Voltammetry (CV) investigations, both DCF and MFA formed electroactive films during repeated scans, with distinct growth mechanisms influenced by scan rate, pH, oxygen presence, and electrode material. Electrochemical Impedance spectroscopy (EIS) and Scanning Electron Microscopy (SEM) investigations confirmed the presence of conductive film formation.

Similar initial redox profiles were exhibited by both DCF and MFA due to their close structural characteristics, but divergence was found in their film formation kinetics. Oxygen was found to inhibit DCF film growth while enhancing the film formed by MFA, indicating opposing roles of oxygen in film formation. Furthermore, both films were found to form only on carbon-based electrode surfaces. The films demonstrated remarkable stability, reversible redox properties and potential for sensing applications. Novel insights were provided into the mechanisms of film formation, dimerization, and oligomerization, supported by UV-Vis Electrochemical-spectroscopy. The film was found to catalyse the electrochemical detection of cationic species like Ferroin indicator and also enabled distinction between DCF and MFA during detection. The growth of the films were further found to be increased through surface modification of the electrode with Nano-particle metal oxides. Moreover, film formation also provided a novel method for the detection of DCF and MFA in trace amounts.

Analysis of Copper-Zinc plating bath on macro and micro electrodes

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Nanoporous copper (NPC) is a high surface area material which has been shown to improve the nucleation, layer growth and dissolution of lithium metal anodes for beyond lithium-ion batteries. By electrodepositing copper and zinc (CuZn) alloy and selectively removing the zinc, a nanoporous copper structure is opened on the surface. Important to this process is the deposition of zinc and copper together in a suitable ratio, which can be controlled by adjusting the plating solution and potential. It was found that different plating solutions were required for plating on macro and micro electrodes. Initially configured for the macro electrode, the micro electrodes required a change in the pH of the solution to achieve the same CuZn results on plating. Conversely, the macro electrode required the addition of saccharin to reduce the risk of delamination but did not require any alteration to the pH of the solution. Understanding of the different requirements for plating on macro and micro electrodes and micro electrodes in this fashion is important for the for future work on transferring results from microelectrode arrays to macro samples in batteries. Microelectrodes can facilitate high rate cycling for accelerated testing of battery materials.

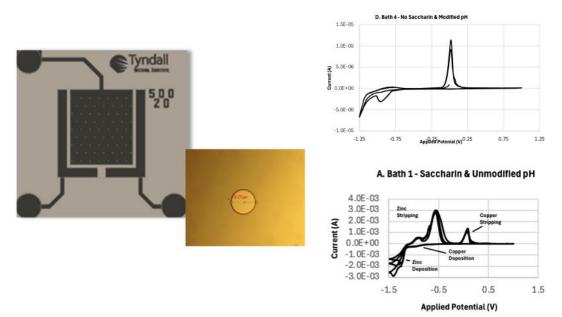


Figure legend left to right: design of microelectrode array, example of individual microelectrode, comparison of CV results for macro and micro electrodes

Investigation of Anti-Corrosion and Self-Healing Properties of Tannic-Based Epoxy Composite Coatings Incorporating Eco-Friendly Cerium-Tyrosine Corrosion Inhibitors

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The corrosion of metals and alloys is a natural phenomenon that has occurred over centuries, but it is becoming more of an impelling issue as the release of metal ions from corroding surfaces leads to environmental contamination. Furthermore, with the emphasis on renewable energy and offshore wind farms, corrosion in marine and offshore platforms, and pipelines is becoming increasingly important. The corrosion of these marine structures does not only lead to structural failure and costly repairs, but also contamination of seawater which will bring potential environmental disasters [1].

The application of organic coatings to metallic-based structures is the traditional corrosion protection method. However, the processing of these coatings relies on solvents and organic components, that are no longer environmentally acceptable and have additional health concerns. Furthermore, organic coatings can be defective with poor adhesion, lack of barrier properties, and inadequate chemical resistance, which allows the corrosive species to penetrate and reach the metal substrates. Accordingly, alternative green materials are urgently needed in corrosion protection systems [2].

In this study an environmentally acceptable coating consisting of tannic-based epoxy (TAEP) with a cerium-tyrosine (Ce-tyr) complex to serve as a corrosion inhibitor, was designed. Both TAEP and ce-tyr were synthesized and characterized through various chemical methods, including Fouriertransform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD). To assess the synergistic effects of these components in reducing the corrosion rate, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) tests were conducted in a 3.5 wt% NaCl solution. The resulting coatings, formulated with varying concentrations of Ce-tyr (0%, 1%, 3%, 6%, and 10% with respect to TAEP namely S0, S1, S3, S6, S10), demonstrated significant potential in reducing the corrosion current density as the amount of ce-tyr increased. Notably, the TAEP composite coating containing 6% Ce-tyr emerged as the most effective sample, achieving a corrosion current density of 1.14×10⁻⁹ A/cm², making it a promising candidate for marine applications and offering a sustainable solution for corrosion protection in marine structures. Immersion tests further indicated that the optimal sample exhibited remarkable resistance over a period of 60 days in the 3.5 wt% NaCl solution; even after being scratched, it maintained its protective qualities against the harsh sodium chloride environment.







2025 Satellite Early Career Researcher Regional Symposium on Electrochemistry (SERRS)

Poster Presentation Abstracts

Characterisation of Glassy Carbon Electrodes Aged in VIV/VV Electrolytes

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Department of Physics and Bernal Institute, University of Limerick

Flow batteries offer a scalable solution for large-scale energy storage, crucial for addressing the intermittency of renewable energy. Among them, the all-vanadium redox flow battery (VRFB) stands out due to its long cycle life, independent energy and power capacity, high energy efficiency, and use of safe, non-flammable aqueous electrolytes. These features, along with low maintenance costs and a green design, make VRFBs an attractive choice for sustainable energy storage1.

The monitoring and optimising of these systems are key to their efficient and rapid operation. The performance of electrodes in vanadium redox flow batteries (VRFBs) is influenced by electrolyte characteristics and electrode treatments2. Enhanced electrodes, with surface modifications or catalysts, show improved electrochemical activity due to increased surface area and better electron transfer kinetics, facilitating efficient redox reactions. In contrast, inhibited electrodes, suffering from passivation, exhibit lower performance with reduced current densities and slower kinetics. These differences are evident in cyclic voltammetry (CV) profiles, where enhanced electrodes have larger peak currents and smaller peak-to-peak separations, indicating higher activity and efficient electron transfer. Understanding these distinctions is crucial for optimising VRFB performance, impacting charge-discharge efficiency, energy density, and stability3. Faster electrode kinetics results in reduced overpotential, and the reaction leads to greater efficiencies in batteries4.

In this poster, we will present and evaluate aged electrode surfaces using advanced techniques, including Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

P01

A solar powered potentiostat for the detection of nitrite and nitrate in environmental samples

^{1*}<u>Matthew McCole</u>, ¹ Martin Bradley, ² Margaret McCaul, ¹ Denis McCrudden *presenter

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The lack of real-time information on nutrient availability in soils has led to excessive use of fertilisers resulting in the pollution of groundwaters and waterways. Conventional analytical techniques provide traceability, precision, and accuracy, but in many cases, they demand expensive and complex instrumentation, but more importantly only provide low analysis frequency.

This study presents a novel solar powered portable potentiostat for rapid accurate detection of nitrate and nitrite in soil pore water for <€30. The system employs a PSoC5 prototyping kit, a single supply Op-amp and a Bluetooth module. Recorded results were comparable to a commercial potentiostat. The PSoC 5LP microcontroller was used as it contains all the necessary components for the fabrication of a potentiostat. The sensing element for nitrate is a carbon screen printed electrode modified with silver nanoparticles whereas a carbon black 3D printed electrode was used for nitrite detection. A linear range of 2.5-200ppm (40-3225µM) and 0.46-46ppm (10-1000µM) was obtained for nitrate and nitrite respectively.

The portability of the system addresses the need for more frequent on-site analysis which facilitates immediate decision-making for environmental researchers and others. The cost effectiveness of the system makes it accessible to a variety of users, especially in resource-constrained agricultural settings.

An electrochemical study of $[PV_2Mo_{10}O_{40}]^{5\cdot}$ doped PEDOT film and its potential as an electrocatalyst towards bromate sensing

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Polyoxometalates (POMs) are versatile "redox-active" materials, and have been used as catalysts in various sensing applications.¹ However, using pristine POMs may have disadvantages, poor conductivity, leaching, degradation, and solubility in aqueous solutions, for instance. Therefore, by forming a composite hybrid material by loading POMs onto various support materials (nanocarbon, metal, and conductive polymers), one can harvest their synergistic superior performances.² Owing to POM/conductive polymer matrix synergy, the following research work is presented. A di-substituted vanadium Keggin type polyoxometalate, [PV₂Mo₁₀O₄₀]⁵⁻, was surface immobilized into the conducting polymer poly(3.4-ethylenedioxythiophene) (PEDOT) onto glassy carbon electrode surface via electropolymerization in an organic media, film abbreviated as PV₂Mo₁₀/PEDOT@GCE. Chronocoulometry was employed to electrodeposit films with different POM loadings. The resulting immobilized hybrid films were characterized by electrochemical technique: cyclic voltammetry. The redox activity of PV2Mo10/PEDOT@GCE was observed within the polymer matrix phase. The hybrid films exhibited a pH-dependent redox activity associated with the polyanion $[PV_2Mo_{10}O_{40}]^{5-}$ and thin layer behaviour up to 100 mV s⁻¹. At an optimized working potential of -0.22 V in chronoamperometric mode, the PV₂Mo₁₀/PEDOT@GCE film can detect bromate at concentrations between 1 μ M and 2000 μ M. Furthermore, the detection limit was determined to be 0.58 µM with no interference from other common ions present in the water.

Mechanistic Investigation of Electrode-Generated Photocatalysts

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The emergence of photoredox catalysis has transformed organic synthesis and energy conversion processes. A fascinating aspect of these systems is their ability to effectively catalyse reactions despite theoretical kinetic limitations suggested by their short-lived excited states (picoseconds to nanoseconds). This work presents a fundamental investigation of electrode-generated photocatalysts, focusing on species that form radical anions or cations capable of acting as super-oxidants or super-reductants upon photoexcitation.

Through systematic electrochemical characterisation using cyclic voltammetry and spectroelectrochemistry, we explore the underlying mechanisms of these transformations. Our investigation reveals that the catalytic process is more intricate than initially presumed, suggesting complex mechanistic pathways that warrant further investigation. The combination of electrochemical and spectroscopic techniques provides unique insights into the redox behaviour and electronic properties of these catalytic systems. By elucidating the basic principles governing these systems, our work aims to establish a stronger foundation for future catalyst design and optimisation strategies in this emerging field.

Photoelectrocatalysis for Resource Recovery from Wastewater

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Wastewater can contain a variety of undesirable contaminants including contaminants of emerging concern (CECs e.g. pharmaceuticals, personal care products, microplastics), organic compounds with high biochemical oxygen demand, and nutrients. Discharge of wastewater to waterways can have serious environmental impacts. However, wastewater may also be viewed as a valuable resource for recovery of value added chemicals, nutrients and energy. For example, the production of hydrogen from wastewater is an appealing option due to its high energy density and use as clean fuel [1,2]. Therefore, development of sustainable treatment technologies combined with resource recovery methods are desirable. Photoelectrochemical systems have emerged as an effective alternative for both contaminant degradation and resource and energy recovery [3]. The overall aim of this research is to investigate the application of nanoengineered electrodes in a photoelectrochemical reactor to degrade organic contaminants including CECs, while simultaneous recovering valuable resources such as metals, phosphate, and hydrogen from wastewater. Initial work has focused on the use of titania nanotube photoanodes produced by anodising titanium metal in the presence of fluoride ions. The morphology and presence of nanotubes was confirmed using FE-SEM. Photoanodes were tested for photocurrent response and the photocurrent density was 130 µAcm⁻² with 0.01 molar Na₂SO₄ as electrolyte, which increased to 220 μ Acm⁻² by using synthesized wastewater under simulated solar irradiation. Further investigation will focus on both anode and cathode reactions, and the design of two compartment photoelectrochemical cells for energy and resource recovery.

Electrochemical Characterisation of Water-Based Deep Eutectic Solvent Electrolytes

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The development of highly concentrated aqueous electrolytes presents unique opportunities for advancing electrochemical technologies. This work investigates quaternary ammonium salts, specifically choline chloride (ChCl) and tetramethylammonium chloride (Me₄NCl), which exhibit exceptional water solubility, enabling the formation of highly concentrated electrolyte systems. At elevated concentrations, these systems can transition into deep eutectic-like states, where strong ion-solvent interactions create unique local environments distinct from traditional aqueous solutions.

Through systematic electrochemical characterisation using cyclic voltammetry and rotating disk electrode studies, we explore how these concentrated environments influence fundamental electrochemical properties and electron transfer processes. Our investigation reveals that these electrolytes exhibit distinct characteristics stemming from their molecular features - notably the hydroxyl group in ChCl and the purely hydrophobic nature of Me_4NCl - which become particularly pronounced at high concentrations.

The fundamental understanding developed in this study provides insights into the behaviour of concentrated quaternary ammonium electrolytes, offering design principles for next-generation electrochemical systems. These findings highlight the potential of these environmentally benign, highly concentrated electrolytes as alternatives to traditional systems, particularly in applications such as energy storage, electrodeposition, and electrochemical sensing.

Miniaturisation and characterisation of an amperometric glutamate oxidase-based composite biosensor for neurotransmitter L-Glutamate monitoring

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A polymer/enzyme composite biosensor for monitoring neurochemical glutamate has been developed and characterised previously by the Lowry group¹. However, to date this and other sensors have predominantly been used for single analyte analysis *in vivo*. In order to facilitate a better understanding of brain function multianalyte chronic studies (> two weeks) of the temporal dynamics of neurotransmitter trafficking in different brain regions are needed. This is now potentially possible given the wide range of biosensors developed for various neurochemicals and with the use of dual enzyme sensors for analytes such as GABA² and choline³. However, multiple sensor implantation, commonly referred to as multiplexing, is needed.

To facilitate multiplexing while minimising cellular damage and foreign body response, it is necessary to miniaturise the currently employed biosensors. However, reducing sensor size reduces the number of sites for enzyme immobilisation resulting in an observed signal much lower than that observed at larger sensors, and a consequent reduction in sensor operational lifetime. To overcome these limitations, platinum black was electrodeposited onto the sensor's surface, increasing its surface area and successfully countering the loss in sensitivity associated with miniaturising.

While this increase in surface area has enabled a reduction in sensor size from 125 μ m to 50 μ m while maintaining a signal large enough for chronic (two week minimum) *in vivo* applications, the developed device needed to be characterised (*in vitro*) to determine if its core properties for *in vivo* monitoring were maintained. The work presented outlines the development and *in vitro* characterisation of this new 50 μ m platinum black polymer/enzyme composite biosensor for glutamate to determine the response time, limit of detection, preform interference testing and ensuring signal integrity across a range of physiological conditions.

Glutathione Sensor Development with the aid of Electrosynthesised Nanogold

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Reactive oxygen species (ROS) are biologically important at low levels as they act as signalling molecules and defend against infections. At high levels they can result in oxidative stress that can cause damage to biomolecules such as enzymes, amino acids, and DNA. To combat high levels of ROS, the body has key molecules that play a part in the antioxidant system [1]. An important non-enzymatic antioxidant is the tripeptide glutathione, which exists in both reduced (GSH) and oxidised (GSSG) form (500:1). Altered ratios are indicative of a number of conditions including neurodegenerative disease [2]. This research focuses on developing an electrochemical sensor for GSH via electrodeposition of nanogold (AuNP) on glassy carbon electrodes. The high surface to volume ratio AuNP surface resulted in a quantitative GSH signal over the range 100 to 500 ^[2]M and surface analysis confirmed the shape and size (68 nm to 537 nm) of the electrodeposited particles. Carbon nano onions (CNOs, concentric multilayered fullerenes consisting of graphitic shells [3]) and the conducting polymer, poly(3,4-ethylenedioxythiophene, [4] are under investigation as underlying conducting support layers for AuNP formation. Work to date has included a loading study for drop casted suspensions of CNO and optimisation of AuNP electrodeposition conditions on both bare and modified surfaces.

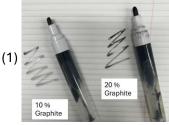
A Non-invasive Wearable Microfluidic Device for Capture and Quantitative Analysis of Glucose Coupled with Skin Electrodermal Activity

<u>Aoife Newman</u>, Benne Dirk Johannes Fennema and Eithne Dempsey Kathleen Londsdale Institute of Human Health, Chemistry Department, Maynooth University, Maynooth, Co. Kildare, Ireland.

A multiparametric, non-invasive wearable microfluidic device for diabetic health monitoring is proposed based on a bespoke biocompatible graphite ink formulation (Gink) that is both writable (Fig.1) and printable. The Gink enables immobilisation of glucose oxidase (GOx)via a 'layer-by-layer' approach and the encapsulation of heterocyclic quinoid species 1,10-Phenanthroline-5,6-dione¹ via enzymatic polymerisation, acting as a proton and electron acceptor for GOx-FADH₂ cofactor regeneration. Surface characterisation of the Gink was accomplished via FTIR, thermal analysis (TGA/DSC) and scanning electron microscopy. Voltammetric and pulse techniques are employed for analytical performance evaluation at the targeted physiological glucose levels in sweat (10-200 μ M²). The optimum method was transferred from glassy carbon to a carbon cloth electrode (Fig. 2) and glucose response obtained at pH 6 via monitoring the electrocatalytic cathodic redox process.

The modified carbon cloth electrode will act as the sensor surface inside a multifaceted epidermal 'smart-patch' which will incorporate a microfluidic "wicking" system for perspiration collection and delivery. A prototype electronic control system involves a customisable Arduinobased potentiostat ³ with off-the-shelf electronic components capable of recording galvanic skin sensor responses (GSR) being related to conductivity and perspiration production ⁴.

(2)



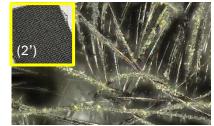


Figure 1: Picture demonstrating the writability of Graphite Ink in refillable pens. Figure 2: Modified carbon cloth threads shown at 50 μ m via KEYENCE VHX-7000 Microscope with insert (2') showing a piece of carbon cloth on the bench

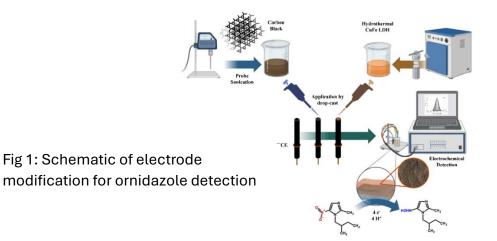
Electrochemical Detection of Ornidazole by means of Copper-Iron layered double hydroxide and Carbon Black-modified electrode

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Ornidazole is a 5-nitroimidazole antibiotic that is heavily employed in the treatment of both human and animal infections [1]. However, it's widespread use amongst the public and the agriculture sector has led to the accumulation of the antibiotic in aquatic environments posing a serious health risk due to its toxicity and the risk of anti-microbial resistance [2]. Thus, novel and green methods of rapidly and accurately detecting its presence in the environment are vital to mitigate its harmful effects.

In this study two environmentally friendly materials are combined to enhance the conductivity and sensitivity of a glassy carbon electrode sensor. Carbon black, functionalised using a novel green method, is layered onto the electrode surface, and then decorated with a hydrothermally synthesised layered double hydroxide (LDH) composed of copper and iron. The sensor shows a significantly improved sensitivity compared to glassy carbon and is capable of detecting Ornidazole concentrations as low as 10 nM up to 260 μ M, displaying excellent stability over multiple uses. Characterisations with SEM, XRD, XPS, and FTIR were conducted as well as pH studies, interference, and real water analysis to display the suitability of the sensor to real-world applications.



Synthesis of Layered Double Hydroxide – Transition Metal Dichalcogenide composites for applications as an electrocatalyst for the oxygen evolution reaction (OER)

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Water splitting is a highly relevant research area aimed at addressing climate change. The reaction yields oxygen and hydrogen, with hydrogen having the potential to serve as a high-density fuel, potentially replacing fossil fuels. Water splitting involves two half-cell reactions: the hydrogen evolution reaction and the oxygen evolution reaction (OER). The OER requires a high overpotential, and there is a clear need to develop new non-precious metal electrocatalysts that can reduce this overpotential.

In this project layered double hydroxides (LDHs) were selected. LDHs are ionic compounds consisting of a layered structure of positively charged sheets with an interlayer containing the corresponding anions, as illustrated in the figure. They can be composed of different transition metals (e.g. Co, Fe or Ni) that are known to be efficient in the OER.

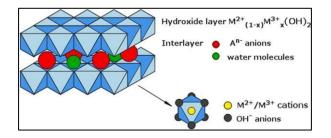


Figure 1: Schematic showing the structure of LDHs.

In this study the CoFe LDH was synthesised and studied, with this material having strong OER activity. The CoFe LDH was then paired with MoS, a well-known semiconductor, to enhance the electrical conductivity of the LDH. This composite was immobilized onto nickel foam electrodes and used as an electrocatalyst for the OER.

Nickel boride/transition metal dichalcogenides as potential bifunctional electrocatalysts for water splitting

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The development of efficient and sustainable bi-functional electrocatalysts for the Hydrogen and Oxygen Evolution Reaction (HER/OER) is critical to advancing renewable hydrogen production technologies. In this study, we synthesised innovative transition metal dichalcogenide (TMD)based heterostructures to address the challenges of cost, stability, and catalytic efficiency. Using a straightforward wet-chemical synthesis method, we combined MoS₂ and MoSe₂ with transition metal borides (Ni_xB), resulting in advanced materials such as Ni_xB@MoS₂, Fe-Ni_xB@MoS₂, and tannic acid-exfoliated MoS₂ nanosheets (ta-MoS₂-ns). These materials were systematically evaluated for HER activity under alkaline conditions (1.0 M KOH), employing glassy carbon electrodes (GCE) and carbon cloth substrates. The carbon cloth, with its high surface area and flexibility, enabled efficient catalyst deposition using methods such as dipping and slurry coating with binders. Comprehensive electrochemical tests demonstrated robust HER performance, with long-term stability observed over operational periods ranging from 1 to 24 hours. These results underscore the synergistic interplay between TMDs and transition metal borides, providing insights into optimising heterostructures for alkaline water splitting. This work highlights the promise of TMD-based materials as scalable, cost-effective, and sustainable electrocatalysts, contributing to the advancement of clean energy technologies.

Combating prozone effect and predicting dynamic range of nanoplasmonic biosensors through capture bioentity optimisation

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Accurately quantifying high analyte concentrations is challenging due to the common prozone effect seen in sandwich assays used in plasmonic nanoparticle-based lateral flow devices (LFDs). Consequently, LFDs are often perceived as less reliable compared to other biosensors, raising concerns about their specificity and sensitivity for the target analyte. To tackle this issue, we present an analytical model designed to predict the prozone effect and the resulting dynamic range of the biosensor based on the concentration of the capture antibody. To validate our model, we conduct a sandwich immunoassay to detect C-reactive protein (CRP) in a phosphate-buffered saline (PBS) buffer using an LFD. Our investigation examines the relationship between the CRP dynamic range and the prozone effect in relation to varying capture antibody concentrations, from 0.1 to 2 mg/mL. The experimental findings support our analytical model, demonstrating that increasing the capture antibody concentration enhances the dynamic range. This model has the potential to broaden the measurable range and lower costs associated with biomarker quantification in various diagnostic assays. Ultimately, this advancement could improve the clinical relevance and reliability of LFDs before the prozone effect becomes a limiting factor.