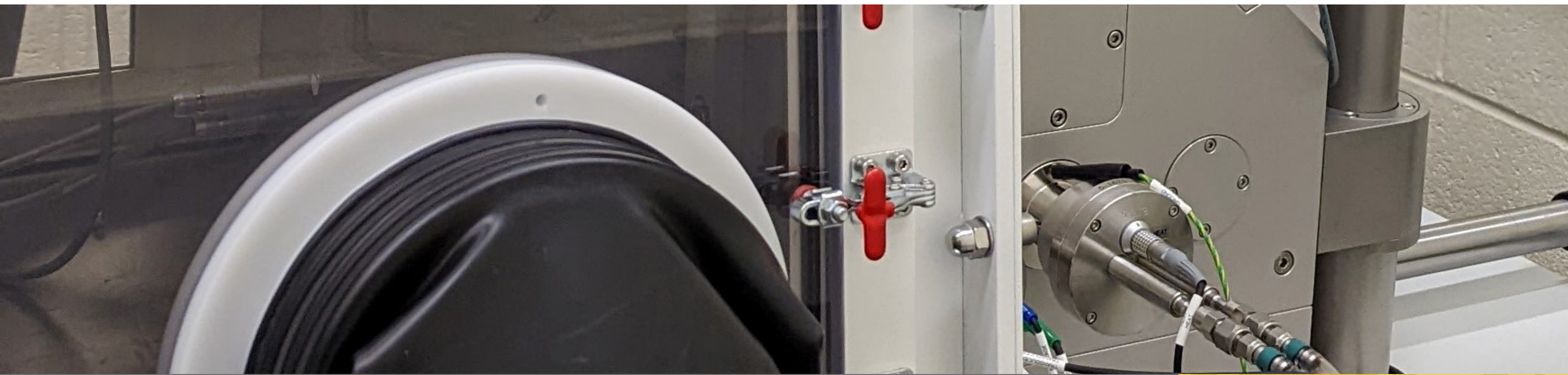
ADVANCED MATERIALS RESEARCH & INNOVATION

UNIVERSITY OF OXFORD

SEM AND EDS ANALYSES OF INORGANIC ELECTRIDES

Moisture and air sensitivity is one of the main challenges to both synthesising and characterising inorganic electrides. To overcome this, previously, Ca_2N samples have been transferred to electron microscopes using N_2 filled glovebags,[1] but such transfer methods are time consuming and do not ensure an airtight environment, which can be detrimental to sensitive samples.

Although electrides were first conceived over 100 years ago with the discovery of 'solvated electrons', the number of inorganic electrides realised experimentally to date still amounts to a little more than a handful. Success in this project will lead to new electride materials, a firmer understanding of electride function and to mechanisms to optimise key chemical and physical properties.



Electrides are exotic materials that typically have electrons present in well-defined lattice sites, and the electron concentration is high enough to allow them to interact with each other.[2] As a result, electrides often show high electrical conductivities and low work functions. However, due to the nature of the unbound electrons, a common problem with electrides is their water/moisture sensitivity. For example, the sub-carbides, RE_2C, RE = Y, Gd-Er and sub-nitrides Ae_2N, Ae= Ca-Ba decompose in moist air, releasing H_2 and CH_4/NH_3, respectively, which present inherent difficulties in characterising such materials, specifically using electron microscopy techniques.

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UNDERPINNING RESEARCH

The project team recognised Ca_2N (space group R-3m) as an "excess electron" compound[3], and a study using ARPES confirmed its electride nature in 2016.[4] This project argues from the premise that electrides should be classified collectively, synthesised by design principles and scrutinised as cutting edge materials.

ROYCE SUPPORT

The samples were mounted at Glasgow prior to measurements, using adhesive carbon tabs in acontinuously purified Ar-filled glovebox. The Al pin stubs were transferred to glass vials with additional parafilm around the lid, and placed inside a DURAN GL45 laboratory glass bottle sealed with a bromobutyl rubber closure, which provides a gas tight seal that is essentialy impermeable to most gases. The glass bottles were then taken out of the glovebox and vacuum sealed in plastic bags. Following transport to Oxford, the samples were transferred into an Ar atmosphere using the Royce *TESCAN MIRA3 SEM integrated with a MBraun Glovebox.*

The Royce equipment allowed the team to analyse air and moisture sensitive materials, finding that the oxygen content decreased significantly in the sample mounted at Oxford compared to the sample mounted in Glasgow, as shown by EDS, meaning there could have been interaction with the adhesive carbon stubs. To decrease the oxygen content observed in EDS analyses, we suggest loading the sample directly at Oxford using vacuum dried carbon tabs.

IMPACT

A firmer understanding of the structure-property relationships in inorganic electrides will pave the way to delivering new materials for energy conversion & storage (thermoelectrics, secondary batteries), electronic applications (field emission, superconductivity, plasmonics) and catalysis (promoting reduction, H transfer, N_2 fixation).

The synthesis of new 'electrenes' via exfoliation of bulk electrides is being worked on as a result of this work.

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4. *J. S. Oh, C.-J. Kang, Y. J. Kim, S. Sinn, M. Han, Y. J. Chang, B.-G. Park, S. W. Kim, B. I. Min, H.-D. Kim and T. W. Noh, J. Am. Chem. Soc., 2016, 138, 2496-2499.*

This project made use of the TESCAN MIRA3 SEM integrated with a MBraun Glovebox, part of the Henry Royce Institute in the David Cockayne Centre for Electron Microscopy at the University of Oxford

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IMAGE

1. TESCAN MIRA3 SEM integrated with a MBraun Glovebox
2. The samples were transported in vacuum sealed plastics bags, with each pin stub triple sealed.

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