The Power of Interfaces:
Fundamentals for Solid State Devices

The Royal Society
10th – 11th March 2020

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General Information

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Royal Society Tour:
A tour of the royal society and its archives is available at 9AM on Tuesday 10th. Places are *very limited,* and attendees will be admitted on a *first come first serve basis*. There will be a sign-up sheet at the registration desk between 8.30 – 9.00AM.

Name badges:
Name badges will be provided at the registration desk. ***You will be required to wear your name badges at all times within the Royal Society.***

10TH MARCH - SESSION 1: The gas/solid interface

Chair: Stephen Skinner	
09.00	Welcome Coffee
09.15	Opening remarks by John Kilner
Plenary 09.30	***"Towards a better mechanistic understanding of electrocatalytic phenomena at oxide / gas interfaces"*** *Jurgen Fleig, TU Vienna*
Invited 10.15	***"In-situ Probing Catalyst Generation and Deactivation with Ambient Pressure X-ray Photoelectron Spectroscopy"*** Bilge Yildiz, Massachusetts Institute of Technology
Invited 10.45	**"Intensified catalysis in solid-state electrochemical reactors"** José Serra, Universitat Politècnica de València
11.15	Coffee Break / Posters 1
Chair: Thomas Lippert	
Invited 11.45	***"Strategies for enhancing oxygen reduction kinetics in SOFC cathodes"*** Katherine Develos-Bagarinao, AIST
12.15	Alexander Stangl (abstract Page 25)
12.30	Özden Celikbilek (abstract Page 26)
12.45	Dino Klotz (abstract Page 27)
13.00	Lunch / Posters 1

10TH MARCH - SESSION 2: The solid/solid interface

Chair: Albert Tarancon	
Plenary 14.00	***“Thermodynamic treatments of space-charge zones at grain boundaries in ionic solids”***
	Roger De Souza, Aachen University
Invited 14.45	***“Solid Electrolytes for Batteries: Atomic-Scale Insights into Ion Conduction and Grain Boundary Effects”***
	Saiful Islam, University of Bath
Invited 15.15	***“First principles, Microkinetic, and Monte Carlo studies on Catalytic reactions at Solid-Solid interfaces and Fast Hydride conduction in bulk”***
	Tomofumi Tada, Tokyo Institute of Technology
15.45	Coffee Break / Posters 1
Chair: Hiroshige Matsumoto	
Invited 16.15	***“Tailoring the Surface Chemistry of Oxide Catalysts and Electrocatalysts via Atomic Layer Deposition”***
	Steve McIntosh, Lehigh Univeristy
16.30	George Harrington (abstract Page 28)
16.45	Francesco Chiabrera (abstract Page 29)
17.00	Ji Wu (abstract Page 30)
17.30 – 19.00	Drinks Reception Posters 2

11TH MARCH - SESSION 3: The solid/solid interface

Chair: Roger de Souza	
09.00	Welcome Coffee
09.15	Introduction by JSPS members
Plenary 09.30	***“Interface analysis in the scanning transmission electron microscope”***
	David McComb, Ohio State University
Invited 10.15	***“Interface Engineering and Understanding of Perfect Perovskites from Strongly Correlated Oxides to Ionics”***
	Judith Driscoll, University of Cambridge
Invited 10.45	***“Self-organised interfaces, crystal chemistry and oxygen mobility in mixed conductors for energy applications”***
	Matthew Rosseinsky, University of Liverpool
11.15	Coffee Break / Posters 2
Chair: Tatsumi Ishihara	
Invited 11.45	**“The dynamic metal anode/solid-electrolyte interfaces in solid state batteries”**
	Ainara Aguadero, Imperial College London
12.15	Federico Baiutti (abstract Page 31)
12.30	Kwati Leonard (abstract Page 32)
12.45	Aleksandra Mielewczyk-Gryń (abstract Page 33)
13.00	Lunch / Posters 2

11th MARCH - SESSION 4: Devices

Chair: Monica Burriel

Invited 14.00	***“Nanomaterials and interfaces for solid state energy microdevices”***
	Albert Tarancon, Catalonia Institute for Energy Research
Invited 14.30	***“Development of Ceres Power’s Steel Cell ® technology: The revolutionary power of ceria on steel for multiple global applications”***
	Shubi Mukerjee, Ceres Power
15.00	*Closing remarks and talk/poster prize ceremony*
15.15	Leaving Tea / coffee

Invited Talks

Day 1 – 10th March

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Day 2 – 11th March

Early Career Talks

Posters Session 1

Photovoltages in perovskite-type oxide thin film cells
Maximilian Morgenbesser

Grain boundaries as a detrimental interface for the electron mobility in ZnO:Al thin films deposited by atmospheric pressure Spatial Atomic Layer Deposition? A new model to link electrical properties and deposition conditions
David Muñoz-Rojas

The origin of high interfacial resistance in Na metal / NaSICON All-Solid-State Batteries: untangling surface chemistry and interface contact effects
Edouard Querel

Study of the oxygen diffusion behaviour of $(La_{0.8}Sr_{0.2})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ *A-site deficient perovskites in humid conditions*
Zijie Sha

Chemical degradation processes in the bulk and at the interface of cathodes materials for lithium ion batteries
Zonghao Shen

Crystal structure analysis of the oxide ion conductor $BaNdInO_4$ *by high-temperature neutron diffraction*
Hitomi Shiga

Posters Session 2

Development of nanostructured ceramic thin films as hydrogen electrode for micro solid oxide cell applications
J. Sirvent

UV induced composition changes in $SrTiO_3$ *and their consequences*
Alexander Viernstein

Investigating Ruddlesden-Popper (n=1) oxide materials for hydrogen production via chemical looping water splitting
George Wilson

New Structure Family of Oxide-ion Conductors Based on $BaGdInO_4$
Hiroshi Yaguchi

Discovery of a Rare-Earth-Free Oxide-Ion Conductor $Ca_3Ga_4O_9$ *by Screening through the Bond-Valence Method and Experiments*
Yuta Yasui

Oxide-Ion Conduction in the Dion−Jacobson-Type Layered Perovskite
Wenrui Zhang

Towards a better mechanistic understanding of electrocatalytic phenomena at oxide / gas interfaces

Juergen Fleig [(a)]

[(a)] Institute of Chemical Technologies and Analytics, TU Wien, Vienna, Austria

Solid oxide fuel or electrolysis cells are based on electrochemical reactions at oxide surfaces such as oxygen reduction or water splitting, and the corresponding cell performance depends crucially on the electrocatalytic properties of the electrode / gas interfaces. Also in many other fields the kinetics of oxygen exchange reactions at surfaces is essential, e.g. for sensors or permeation membranes. This leads to much interest in reaction mechanisms of the corresponding reactions. In a first step, often the relevant geometric reaction pathway (via triple phase boundaries or via the electrode bulk) is identified and the most resistive region within the predominant pathway is localized (e.g. a certain interface or the electrode bulk). In a next step, it is desirable to obtain an atomistic understanding of the resistive or electrocatalytic processes. Here, exact surface species or point defects and phenomena such as dissociation or ionization come into play, and despite substantial research activities many questions remained unsolved so far.

This talk presents our recent progress on this topic: Established electrochemical approaches (e.g. Butler-Volmer equation) are often not appropriate for describing such reactions and a novel model was thus developed, which allows a proper interpretation of $p(O_2)$ dependences and current-voltage curves. It is discussed, how composite electrodes can improve the reaction rate by a kind of "job sharing". Exsolution-based composites are considered at the fuel side (Fe on LSF) and it is discussed, what happens during electrochemical switching of their electrocatalytic activity by an overpotential. Moreover, it is illustrated how nano-particles of Pt on $(La,Sr)FeO_3$ (LSF) thin film electrodes strongly improve the reaction rate of oxygen reduction and also completely change the reaction mechanism and the $p(O_2)$ dependence. Finally, the topic of active sites and electrode degradation is considered, with special emphasis on $(La,Sr)CoO_3$ (LSC) and LSF. Extraordinarily high oxygen reduction activity of pristine thin films is shown, different reasons for degradation are discussed, and surprising defect chemical phenomena are displayed for oxygen evolution from LSC thin films.

In-situ Probing Catalyst Generation and Deactivation with Ambient Pressure X-ray Photoelectron Spectroscopy

Bilge Yildiz(a,b) *, *Jiayue Wang*(a), *Alexander K. Opitz*(a,c),

(a) Department of Nuclear Science and Engineering, MIT, Cambridge, United States
(b) Department of Material Science and Engineering, MIT, Cambridge, United States
(c) Institute of Chemical Technologies and Analytics, TU Wien, Vienna, Austria

Catalysts design plays a crucial role in both energy storage and fuel synthesis. To enable a precise description of the catalytic reactions, *in situ*characterization of surface chemistry is inevitable. In this talk, I am going to present our recent efforts in using ambient pressure X-ray spectroscopy (APXPS) to understand both the catalyst generation and deactivation under real working conditions.

A recent advance in catalyst design is to exsolve metal nanoparticles at the surface of a supporting oxide. Unlike traditional deposition techniques, the nanoparticle catalysts from exsolution are anchored in the parent oxide, which makes the exsolved nanoparticles more resistant against particle agglomeration. While being a promising pathway, the exsolution efficiency requires further improvement. In the first part of this talk, I will demonstrate the capability to enhance exsolution with biaxial lattice strain on epitaxial $La_{0.6}Sr_{0.4}FeO_3$ thin films. Coupling surface chemical information from APXPS with morphological information from electron and atomic force microscopy, we found that both surface coverage and dispersion of the exsolved Fe^0 particles can be significantly enhanced with biaxial tensile strain.

Regarding catalysts deactivation, carbon deposition from CO and other carbon-containing fuels (“coking”) is a major cause of the performance degradation of catalysts and electrocatalysts in many energy conversion devices. In the second part of the talk, I will present our investigation into the relationship between gas/solid interface compositional and operational factors that lead to the onset of carbon deposition on thin-film CeO_2 electrodes at 450 °C in CO/CO_2 atmosphere. During the measurement, electrical bias was applied to drive the redox reaction as well as to change surface oxidation state. With *in-operando* APXPS, we tracked the evolution of surface chemical change during carbon deposition on ceria-based thin-film samples. The surface spectroscopy analysis yielded information about the relationship between carbon deposition, surface defect concentration and surface composition.

Intensified catalysis in solid-state electrochemical reactors

Jose Serra *(a)*

(a) Instituto de Technología Química, Universitat Politècnica de València

The gas exchange and catalytic pathways on the surface of solid-state devices is usually determining the evolution rate (nominal current density) but also the selectivity towards different final reaction products and stability of the system. Solid-state ionic materials are a key component in today's and future energy interconversion as in fuel cells, batteries and electrolyzers. Beyond this application, the application of solid-state ionic conductors in process industry is becoming very relevant and will become indispensable in the transformation of energy to minimize CO_2 footprint via electrification of process units. Electrochemical solid-electrolyte cells enable the design of catalytic reactor processes that shift chemical equilibria favorably and facilitate separation of valued-products. The concept of electrochemically-driven catalytic reactors based on ceramic ion-conducting cells will be presented, where selective electrocatalyst are require to drive the reaction through a preferred pathway, thus, producing selectively a gas product. For instance, protonic membrane reactors allow the intensification of equilibrium-limited reactions where H_2 participates. Ceramic proton conductors based on tungstates or doped $BaZrO_3$ possess high chemical stability in carbon-containing atmospheres and high proton conductivity. This enables process intensification through integration of the catalytic reactions and separation in one process step, producing pressurized H_2. Beyond equilibrium shift that enables reaching higher per-pass yield of the target product, other remarkable intensification mechanisms can be implemented in the reactor, leading to unprecedented energy efficiency and catalyst stability. One effect is related to the micro-thermal integration at both sides of the solid-state conductor, i.e. by coupling physio-chemical exothermic and endothermic process Another effect is related to the concomitant transport of oxide-ions through the electrolyte, enabling to control the coke formation or oxidative catalyst decay, depending on the specific process. The overall rate of protons and oxide-ions can be tuned by adjusting the catalytic properties of the electrode. The use of co-ionic assemblies is exemplified in the methane dehydro-aromatization (MDA) process, strongly limited by equilibrium and coking.

Strategies for enhancing oxygen reduction kinetics in SOFC cathodes

Katherine Bagarinao (a)

(a) National Institute of Advanced Industrial Science and Technology, Tokyo, Japan

Novel materials for application as cathodes in solid oxide fuel cells (SOFCs) are currently being investigated to achieve superior electrochemical performance and overcome the sluggish oxygen reduction kinetics at lower operating temperatures. In this presentation, I will discuss some strategies explored by our group to enhance oxygen reduction kinetics in SOFC cathodes, specifically, tuning of cathode microstructures at the nanoscale level and utilization of multilayering approaches to leverage the effect of heterointerfaces on oxygen incorporation.

Thermodynamic treatments of space-charge zones at grain boundaries in ionic solids

Roger A. De Souza [(a)]

[(a)] Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

In contrast with the bulk phase, an extended defect (dislocation, grain boundary, surface, domain wall) in an ionic solid is not constrained in equilibrium to remain locally electroneutral. Because of interactions between the extended defect and point defects, the extended defect will in general become electrostatically charged, with the adjacent bulk phase concomitantly developing diffuse, enveloping space-charge zones.

The altered concentrations of point defects in these space-charge zones have long been understood to affect, for instance, the transport of charge across grain boundaries in polycrystalline systems. In this presentation, I will draw attention to three aspects that have received far less attention: that space-charge zones can affect the excess Gibbs free energy of a grain boundary [1,2]; that concentrated solid solutions cannot be treated with the standard Poisson–Boltzmann approach [3,4]; and that space-charge zones can provide an unusual contribution to accelerated diffusion along grain boundaries [5]. Throughout the presentation, I will emphasise the need to consider space-charge zones from a thermodynamic perspective.

[1] R. A. De Souza, *Phys. Chem. Chem. Phys.* **11** (2009) 9939.
[2] R. A. De Souza and E. C. Dickey, *Phil. Trans. R. Soc. A* **377** (2019) 20180430.
[3] D. S. Mebane and R. A. De Souza, *Energy Environ. Sci.* **8** (2015) 2935.
[4] X. Tong, D. S. Mebane and R. A. De Souza, *J. Am. Ceram. Soc.* **103** (2020) 5.
[5] J. P. Parras and R. A. De Souza, in preparation.

Solid Electrolytes for Batteries:

Atomic-Scale Insights into Ion Conduction and Grain Boundary Effects

Saiful Islam (a)

(a) Department of Chemistry, University of Bath, Bath BA2 7AY, UK

In the critical area of sustainable energy storage, solid-state batteries are attracting considerable attention due to their potential safety, energy-density and cycle-life benefits [1]. A complete understanding of solid electrolyte materials for lithium- and sodium-ion batteries requires greater fundamental knowledge of their structural, ion transport and interface properties. For example, grain boundary effects on ion transport in oxides versus sulfides are not fully understood on the atomic-scale. This talk will highlight recent studies [2-4] on Li-ion and Na-ion conduction mechanisms, surface structures and grain boundaries in oxide, oxy-halide and sulfide based solid electrolyte materials.

[1] T. Famprikis et al., *Nature Mater.*, 18, 1278 (2019).
[2] J.A. Dawson et al., *Chem. Mater.*, 31, 5296 (2019)
[3] J. A. Dawson et al., *J. Am. Chem. Soc.*, 140, 362 (2018).

First principles, Microkinetic, and Monte Carlo studies on Catalytic reactions at Solid-Solid interfaces and Fast Hydride conduction in bulk.

Tomofumi Tada (a,b)

(a) Kyushu University Platform of Inter/Transdisciplinary Energy Research,
(b) Kyushu University, 744 Motooka, Nishi-ku, 819-0395 Fukuoka, Japan

Recently, computers and computational algorithms have been developed rapidly, and computational materials designing has grown up as a fundamental research tool in the field of materials science. In particular, first-principles electronic structure calculation is one of the most reliable computational tool for both known and unknown materials. In addition, state-of-the-art algorithms such as Monte Carlo sampling, genetic algorithm, neural network as machine learning, etc, have been extending the search area of materials and size-and-time domains of dynamics in materials. In this talk, we select three topics as examples; the first one is the first principles microkinetic study on ammonia synthesis at the Ru/hydride interface [1], and the second one is the first principles molecular dynamics simulation for the fast hydride conduction in H-substituted La_2O_3 [2]. We also briefly introduce a full-atomistic kinetic Monte Carlo dynamics that can handle atomic-scale dynamics in large-size and long-time domains [3].

[1] T. Nakao, T. Tada, and H. Hosono, *J. Phys. Chem. C,* in press (10.1021/acs.jpcc.9b10850).
[2] K. Fukui, S. Iimura, T. Tada, S. Fujitsu, M. Sasase, H. Tamatsukuri, T. Honda, K. Ikeda, T. Otomo, and H. Hosono, *Nat. Commun*., **10**, 2578 (2019).
[3] T. Tada, *ECS Trans.*, **78**, 2815-2822 (2017).

Tailoring the Surface Chemistry of Oxide Catalysts and Electrocatalysts via Atomic Layer Deposition

Steven McIntosh (a)

(a) Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, PA 18015, USA

The outermost surface chemistry of mixed metal oxide catalysts and electrocatalysts dictates their catalytic activity and selectivity. A well studied example of this is in solid oxide electrochemical cells where the elemental composition of the surface can differ markedly from the bulk due to surface segregation at elevated operating and synthesis temperatures. While this can be advantageous if correctly tuned, for example, to evolve well distributed and anchored catalytic nanoparticles, it is more commonly detrimental to performance. A significant barrier to strengthen our understanding of these surfaces has been a lack of adequate tools to synthesize porous materials and electrode structures with controlled surface chemistry.

Atomic layer deposition (ALD) enables controlled, sub-monolayer conformal coating of mixed metal oxide films and is commonly utilized in a flow-through configuration for layer-by-layer growth on planar substrates. Our modified ALD approach utilizes a cyclic batch deposition process that allows sufficient time for precursors to diffuse into pores, thus enabling conformal coating of powders and porous electrode substrates. When coupled with outer-surface composition analysis via high-sensitivity low energy ion scattering (HS-LEIS), and measurements of catalytic and electrocatalytic performance, this approach provides significant new understanding of the role of surface chemistry, and enables the fabrication of unique, highly active, materials. Applications in both catalysis and electrocatalysis will be presented.

Interface analysis in the scanning transmission electron microscope

David W McComb [(a,b)]

[(a)] Dept of Materials Science & Engineering, The Ohio State University, Columbus, OH 43210
[(b)] Center for Electron Microscopy & Analysis, The Ohio State University, Columbus, OH 43212

High angle annular dark field (HAADF) imaging in scanning transmission electron microscopy has been extensively used for probing solid interfaces for many years, with many examples of atomic position imaging with picometer precision. The development of direct electron detectors has resulted in new approaches to interface characterization such as 4D-STEM and integrated differential phase contrast that can allow determination of the positions of light elements such as oxygen with similar precision. The same detector technology has delivered vastly improved electron energy-loss spectroscopy capabilities which, when combined with monochromated sources, allow coordination environment, bonding and electronic structure to be probed with much enhanced signal-to-noise ratio. In this contribution I will review these recent developments and illustrate how these new imaging and spectroscopy methods are revealing new insights at interfaces in structural and functional materials.

Interface Engineering and Understanding of Perfect Perovskites from Strongly Correlated Oxides to Ionics

Judith Driscoll (a)

(a) University of Cambridge, UK

Strongly correlated perovskite interfaces have led to emergent effects including the discovery of 2DEGs, new ferroelectrics, magnetics and superconductors, etc. Interface charge transfer, orbital and atomic reconstructions can explain these effects. Interesting interface phenomena also occurs in ionic systems and the question it interesting to ponder whether there is a link to aforementioned effects. In this work, we grow both perfect epitaxial planar superlattice structures and self-assembled vertically aligned nanocomposites to learn about the interfaces in ionic systems. We probe these interfaces using a wide range of characterisation tools and using theoretical calculations. We find that ionic interfaces have both modified ionic conduction (solid-solid interfaces) and catalytic effects (gas-solid interfaces) arising from structural and chemical effects at interfaces.

Self-organised interfaces, crystal chemistry and oxygen mobility in mixed conductors for energy applications

Matthew J. Rosseinsky (a)

[a] Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

It is demanding to achieve the multiple functionality required of an electrode or membrane within a single phase, and hence there has been considerable focus on synthetic composites with interfaces between materials of distinct compositions and structures. Our work has focussed on understanding and controlling the nature of these interfaces. This presentation will address the self-organised assembly of coherent interfaces between isostructural perovskite phases which then co-operate to function as stable low ASR SOFC cathodes (1,2). A range of techniques establish the chemical mechanisms that control the phase separation. The understanding of the mechanisms controlling the interfaces between non-isostructural phases is less advanced, and we have shown that in thin films layer-by-layer two dimensional growth of materials with quite distinct structures can be enforced by considering the extent of chemical bonding as well as geometrical mismatch (3). The strong influence of specific chemical factors on ion mobility and stability under application conditions is demonstrated by the high oxygen mobility and CO_2 tolerance of a recently evaluated perovskite containing Bi^{3+}. (4)

(1) Demont et al., J. Am. Chem. Soc. **135**, 10114, 2013
(2) J.F. Shin et al., Nature Energy **2**, 16214, 2017
(3) M. O'Sullivan et al., Nature Chemistry **8**, 347, 2016
(4) M. Li et al., Advanced Materials **32**, 1905200, 2020

The dynamic metal anode/solid-electrolyte interfaces in solid state batteries

Edouard Querel [a], *Rowena Brugge* [a], *Federico Pesci* [a], *Andrea Cavallaro* [a], *Rrichard Chater* [a], *Ainara Aguadero* [a]

[a] Imperial College London, UK

Safety issues of state-of-the-art liquid flammable electrolytes-based batteries are promoting a race for the successful integration of commercial solid-state batteries in which the integration of metal anodes, opens the door to higher energy and power densities. However, the development of these systems has been so far hindered by the lack of understanding of the dynamic metal/solid interfaces that leads to chemical, electrochemical and mechanical degradation during cell operation.

In this work, we focus on the study of Na/NaSICON and Li/Garnet interfaces using a combination of electrochemical and surface analysis techniques. We prove that the processing conditions can be tuned to optimise the interface chemistry leading to the apparent suppression of the interfacial resistance for ion exchange. The study also proves that the interface is very dynamic leading to both chemical and microstructural changes that can have important effects on the battery cycle life and performance. Our work highlights the complexity of these systems and propose the need of new *in situ* techniques to gain a deeper understanding of the processes taking place. In this regard, we introduce a novel and beyond state-of-the-art dual secondary ion mass spectrometer (SIMS) aimed at innovative 3D chemical and microstructural analysis with *operando* capabilities.

Nanomaterials and interfaces for solid state energy microdevices

Albert Tarancon (a)

(a) Catalonia Institute for Energy Research, Sant Adrià de Besòs 08930, Spain

The internet of things (IoT) will revolutionise the way in which we interact with the world around us: sensors of temperature, presence, traffic density will measure data and communicate to a control unit for decision-making. Autonomous actions for process optimization, intervention, environmental safeguard will be taken without human intervention.

Embracing the IoT in our lives will require the advent of a new generation of portable power sources. For this, new families of rechargeable and autonomous micro-energy sources offering high specific power (0.5-10 mW and 1-100 J) have to be developed in order to integrate the required power capabilities in the IoT nodes.

These new technologies will be necessarily miniaturizable and likely based on advanced concepts of Nanoionics and Iontronics, i.e. will take advantage of ion-based local effects at the nanoscale. This way, surprising properties of fast conduction and high storage capacity can be obtained. Moreover, by taking advantage of silicon microfabrication techniques, a superior manufacturability, cost-effectiveness and the possibility to host dense structures in a seamless architecture will be reached; all in an environmentally friendly material.

In this talk, we will present the HARVESTORE project devoted to integrate harvesting and storage units based on new concepts in silicon technology while reviewing interesting concepts of Nanoionics and Iontronics.

Development of Ceres Power's Steel Cell® technology: The revolutionary power of ceria on steel for multiple global applications

Dr. Subhasish Mukerjee [(a)]

[(a)] Ceres Power Limited

Ceres Power is developing and commercializing its low-temperature metal supported SOFC technology (the 'Steel Cell') based predominantly around the use of ceria on low cost steel. This unique design architecture allows for a robust, low cost fuel cell product, whilst retaining the advantages of fuel flexibility, high efficiency and low degradation. The technology lends itself to multiple applications in the energy sector.

Over the last few years, several significant technological and commercial developments have taken place. This technology iteration offers higher power, the ability to operate at higher efficiency and state-of-the-art performance degradation rates, whilst retaining the outstanding robustness to thermal cycling, vibration and REDOX cycling characteristic of the Steel Cell technology. Multiple customers and partners are working with Ceres Power to license and develop products for multiple applications globally based on this core technology. This includes customers in Japan, Korea, Germany, China and the USA. This presentation will highlight the progress in the technology, the array of commercial products with this technology and the fast commercialisation of this technology all around the world.

Study of surface oxygen exchange kinetics of $YBa_2Cu_3O_{7-\delta}$ thin films using Electrical Conductivity Relaxation Measurements

Alexander Stangl[1,2], Mónica Burriel[2], Teresa Puig[1]

[1] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain
[2] Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, 38000 Grenoble, France

YBCO films are of great technological interest as they show exceptional good superconducting properties. As in all cuprate superconducting oxides, these properties are governed by the oxygen content of the material. Understanding how to achieve optimal oxygen doping of the oxygen deficient triple perovskite YBCO structure is still an open, critical issue and its optimization a main goal of this work. The oxygenation kinetics is strongly influenced by microstructural and morphological features at the surface. The elementary reaction mechanisms comprise molecular oxygen absorption, ionization, dissociation, incorporation and atomic bulk diffusion.

We show that in-situ techniques as electrical conductivity relaxation (ECR) and high temperature environmental XRD (HTXRD) are very useful tools to analyze the oxygen exchange processes. Thin films studied were obtained by chemical solution (CSD) and pulsed laser deposition (PLD) with thicknesses of 25 to 250nm. We monitor the mechanisms of the oxygen reduction (ORR) and oxygen evolution reaction (OER) in YBCO thin films during post growth thermal treatments by changing between oxidizing and reducing pO2 atmospheres. Our results demonstrate that the ORR in these thin films is limited by surface reactions. This reaction can be catalyzed by sub-micrometer silver particles on the surface.

Further, using a bulk chemical defect model, the pO2 dependence of the surface exchange constant k_{chem} and the initial reaction rate $\mathfrak{R}$ allows to identify the rate determining step as the oxygen-oxygen vacancy recombination at the gas-solid interface. Additionally, we find that strain engineering via film-substrate mismatch impacts surface reactions, likely linked to variations in the oxygen vacancy formation energy.

The understanding the oxygen exchange reactions at the surface enables to tune the carrier concentration via the oxygen stoichiometry, leading to remarkable superconducting properties in these YBCO thin films.

Funding from from EU ERC-AdG-2014-669504ULTRASUPERTAPE, Severo Ochoa SEV2015-0496 program and MINECO MAT2014-51778-C2-1-R and FEDER project is acknowledged.

Surface Restructuring of Thin-Film Electrodes Based on Thermal History and Its Significance for the Catalytic Activity and Stability at the Gas/Solid Interfaces

Ozden Celikbilek[a], Andrea Cavallaro[a], Gwilherme Kerherve[a], Sarah Fearn[a], Ainara Aguadero[a], John A. Kilner[a,b], Stephen J. Skinner[a]*

a. Department of Materials, Imperial College London, Prince Consort Road, London SW7 2BP, United Kingdom

b. International Institute for Carbon-Neutral Energy Research (I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

*Corresponding author: o.celikbilek@imperial.ac.uk

Electrodes in solid-state energy devices are subjected to a variety of thermal treatments, from film processing to device operation at high temperatures. All these treatments have an influence on the chemical activity and stability of the films, as the microstructure and morphology are shaped by the thermally induced chemical restructuring. Here, we investigate the correlation between the oxygen reduction reaction (ORR) activity and thermal history in complex transition metal oxides, in particular, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC64) thin films deposited by Pulsed Laser Deposition (PLD). To this end, three ~200 nm-thick LSC64 films with different thermal history were studied; two films were grown at 100 °C and 750 °C substrate temperatures, respectively and the third one was grown at 100 °C and post-annealed at 600 °C for 4 h in ambient air. Oxygen self-diffusion coefficient (D^*) and oxygen surface exchange coefficient (k^*) were measured by isotopic exchange depth profiling technique coupled with time-of-flight secondary-ion mass spectrometry (ToF-SIMS). A combination of surface-sensitive elemental characterisation techniques (i.e. low-energy ion scattering; LEIS, X-ray photoelectron spectroscopy; XPS and secondary-ion mass spectrometry; SIMS) were employed to thoroughly investigate the cationic distribution from the outermost surface to the film/substrate interface. Moreover, electrochemical impedance spectroscopy was used to study the activity and the stability of the films. Our research has revealed that the thermal history of films greatly affects the microstructure/morphology and the elemental distribution at the interfaces. However, the degradation rates of the films showed a two-fold difference in the long-term tests, despite initially comparable ORR activity. Here, we emphasise the significance of thermal history particularly for the stability of the LSC64 electrodes and propose that it should be considered as among the main pillars in the design of active surfaces.

New Tools to Analyze the Photoelectrochemistry and other Intrinsic Properties of Ceramic Materials

Dino Klotz[1,2]

[1]WPI International Institute for Carbon Neutral Energy Research, Kyushu University, Motooka 744, Fukuoka, Japan
[2]Department of Material Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, USA

Photoconductivity is an important characteristic for any device that relies on a photo-effect. However, it is not easy to distinguish photoconductivity from other effects such as light-enhanced surface exchange or temperature effects. Moreover, the photoconductivity itself can also originate from different charge carriers being excited from different states within the band structure, prone to different recombination mechanisms. Furthermore, temperature itself can modify bandgap, conduction and recombination characteristics. Gaining a full understanding of the processes that generate photoconductivity is not an easy task and involves characterization tools, some of which might require special device architectures and test conditions far from the usual operating conditions.

I will introduce a versatile test setup where model cells can be characterized optically and electrically at the same time, and where important conditions such as temperature, oxygen partial pressure and illumination intensity and wavelength can be varied systematically.

Innovative frequency-domain measurement techniques such as intensity modulated photocurrent/-voltage spectroscopy (IMPS/IMVS) are then applied, which have shown to reveal valuable information about charge carrier dynamics for photoelectrodes and photovoltaic cells *in operando* [1]. To the best of my knowledge, these techniques have never been applied for materials characterization as opposed to device characterization. However, with the small signal light perturbation that is the key element of IMPS and IMVS, it is possible to trigger the light effect directly and analyze the different contributions to the system response by well-known impedance analysis tools.

In this contribution, I will give a brief introduction into IMPS and IMVS and show how these techniques can be applied to model electrodes consisting of STO and STF. The results are compared to EIS under different illumination and we will show how to extract the relevant information about the photo-response. By evaluating the activation energies of the different electrochemical and photoelectrochemical processes, we can attribute those to physical effects. With that, we can clarify some of the previously unknown processes that lead to anomalies observed in STO/STF under illumination and obtain valuable information about other intrinsic properties such as band structure.

This work was supported by JSPS Core-to-Core Program, A. Advanced Research Networks: “Solid Oxide Interfaces for Faster Ion Transport”.

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Interfaces and strain in rare-earth substituted ceria: Modifying defect concentrations and mobilities

George F. Harrington[1,2,3,4], Lixin Sun[4,5], Dmitri Kalaev[4], Sunho Kim[4], Bilge Yildiz[4,5], Kazunari Sasaki[1,2,3], Nicola H. Perry[6,3], and Harry L. Tuller[4,3]*

[1] Next-Generation Fuel Cell Research Centre, [2] Center of Coevolutionary Research for Sustainable Communities (C^2RSC), [3] International Institute for Carbon Neutral Energy Research (I^2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

[4] Department of Materials Science and Engineering, [5] Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge MA 02139, U.S.A.

[6] Department of Materials Science and Engineering and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

*harrington.frederick.george.302@m.kyushu-u.ac.jp

There is a coupling between the chemical, electrical, and mechanical properties in electroceramic materials, referred to as *electro-chemo-mechanics*. Therefore, mechanically confined systems such as thin films may be investigated as a route to improved functional properties, shifting the paradigm of materials development away from compositional tuning and searching for new functional oxides. Rare-earth substituted ceria is an excellent model material to study these effects, and in this presentation, we demonstrate two key experimental findings.

First, we demonstrate that the migration barrier in rare-earth substituted CeO_2 can be modified by lattice strain. Using an unconventional approach to straining films, and careful analysis of the literature, we managed, for the first time, to develop a quantitative consensus on the variation in the transport properties of ceria as a function of lattice strain. We also experimentally demonstrate the effects of migration direction with respect to the biaxially strained plane. We find that the modification is dependent on the size of the dopant cation, showing that defect association plays a substantial role. We rationalise our findings using static force-field simulations, suggesting that the cause is due to a combination of changes in the migration barrier and vacancy-cation configuration.

Second, we explore the extent that charge carrier concentrations in mixed ionic-electronic conductors (MIECs) can by modified at interfaces. Pr substituted CeO_2 (PCO) is an excellent MIEC for fundamental studies as it has been extensively investigated, and the defect chemistry, chemical expansion, transport, and optical properties are well described in the bulk material. By fabricating nano-granular polycrystalline films and multilayer heterostructures, we have investigated the effects of homogeneous and heterogeneous interfaces on the concentration of oxygen vacancies and small polarons. Using a combination of impedance spectroscopy in conjunction with *in-situ* optical transmission measurements, to unambiguously extract the non-stoichiometry, we observe substantial deviations from bulk behaviour in materials dominated by a high density of interfaces. By engineering the density and proximity of interfaces, we demonstrate a lowering in the effective enthalpy for Pr reduction, allowing the non-stoichiometry and density of charge carriers to be tailored.

Interface engineering in $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ thin films by tuning local nonstoichiometry in grain boundaries

F. Chiabrera[1], I. Garbayo[1], F. Baiutti[1], L. López-Conesa[4], A. Kordatos[2], A. Morata[1], A. Ruiz-Caridad[4], M. Núñez, S. Estradé[4], F. Peiró[4], A. Chroneos[2,3], A. Tarancón[1,5]

[1]Department of Advanced Materials for Energy, Catalonia Institute for Energy Research (IREC), Jardí de les Dones de Negre 1, Planta 2, E-08930 Sant Adrià de Besòs (Barcelona), Spain.

[2]Faculty of Engineering, Environment and Computing, Coventry University, Priory Street, Coventry CV1 5FB, United Kingdom

[3]Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

[4]Department of Electronics, University of Barcelona, C. de Martí i Franquès 1, 08028 Barcelona, Spain.

[5]ICREA, Passeig Lluís Companys 23, 08010, Barcelona, Spain

E-mail: fchiabrera@irec.cat

Interface-dominated oxides, e.g. in the form of nanocrystalline thin films, have emerged as enthralling systems for energy and information technologies owing to the large tunability of their functional properties. In particular, it was discovered that grain boundaries in manganites are able to deeply impact the overall material's functionalities by boosting the oxygen mass transport while abating the electronic and magnetic order. In this work, the origin of this remarkable behaviour is assessed. The structural and chemical characterizations of $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ thin films, deposited by pulsed laser deposition, reveal that strained grain boundaries witness a profound modification of the local anionic and cationic compositions. Moreover, it is found that, by tuning the overall cationic content in the thin films (Mn/(La+Sr) ratio), the interface local nonstoichiometry can be purposefully modified, maintaining its oxygen deficiency character yet altering the cationic concentration profiles. Finally, the study of the electrical and electrochemical properties of these interfaces unveils the possibility of tuning the functionalities of manganite thin films by grain boundary engineering.

Acknowledgements

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (ULTRASOFC, Grant Agreement number: 681146)

Revisiting Lanthanide in Oxides – A Quantum Mechanical Insight into their Catalytic Activities

Ji Wu[1], Kotaro Fujii[2], Masatomo Yashima[2], Aleksandar Staykov[3], Taner Akbay[4], Tatsumi Ishihara[3,4,5], John A. Kilner[3,6]

1. Department of Chemistry, University of Bath, Bath BA2 7AX, United Kingdom
2. Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-W4-17, Ookayama, Meguroku, Tokyo, 152-8551, Japan.
3. International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University, 744 Mottoka, Nishi-ku, Fukuoka 819-0381, Japan.
4. Advanced Research Centre for Electric Energy Storage, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
5. Department of Applied Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
6. Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom

Lanthanide containing complex oxides, especially the ABO_3 perovskite and $A_{(n+1)}BnO_{(3n+1)}$ Ruddlesden-Popper series, attract much interest as promising catalytic materials in many renewable energy applications such as electro-chemical energy conversion , hydrogen production and chemical looping devices. Recent experimental and theoretical studies on some members of these materials, e.g. $La_2NiO_{4+\delta}$, revealed that the La-O terminated surfaces are catalytically active under operational conditions. These findings suggested that the conventional understanding of a fully ionized, catalytically inert La^{3+} ion needs to be revised.

By applying generalized gradient approximation and hybrid density functional theory methods were used to study and compare the electronic structures of representative lanthanides (La, Pr) and alkaline-earth metals (Ba, Sr) in related oxides.[1] Consistent results were obtained across different ab initio methods and approaches used. Density of states plots and charge analysis results showed that the lanthanides exhibits a partially occupied d-orbital and a calculated atomic charge of +2 instead of its nominal valence number (+3) in the oxides, while the alkaline-earth metals does not show similar characteristics. Electron density maps obtained from synchrotron X-ray diffraction experiments confirmed the simulation findings as well. The presence of available d-orbital electron on La and associated partial covalency was postulated as being responsible for the catalytic behaviour observed in experiments. Considering the commonality of the lanthanides behaviours in all the simple and complex oxides we studied, we believe that these characteristics should be considered for the general understanding of lanthanides activities in these oxides.

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Ceramic thin film nanocomposites: a playground for energy application

F. Baiutti (1), M. Acosta (2), F. Chiabrera (1), J. Sirvent (1), A. Cavallaro (3), A. Aguadero (3), J. MacManus-Driscoll (2), A. Tarancon (1, 4)

1) Catalonia Institute for Energy Research (IREC), Jardins de Les Dones de Negre 1, 08930 Sant Adria' Besos, Barcelona, Spain
2) Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom
3) Department of Materials, Royal School of Mines, Imperial College London SW7 2AZ, UK
4) ICREA, 23 Passeig Lluís Companys, Barcelona 08010, Spain.

Self-assembled thin film nanocomposites in the form of vertically aligned nanostructures (VANs) have been intensively investigated in the last years, revealing a plethora of surprising functional properties such as enhanced ionic transport and novel interface electronic states. This is ascribed to the nanoscale phase alternation of the phase components, which allows for interface effects to be predominant over the bulk behavior.

In this contribution, the application of such nanostructures for high temperature electrode application is shown in relation to two relevant cases, namely Sr-doped lanthanum manganite (LSM)/fluorite VANs and mesoporous lanthanum ferrite (LSCF).

In the first example, the structural and electrochemical analysis of LSM/doped zirconia and LSM/doped ceria is presented, highlighting a decisive enhancement of the oxygen reduction kinetics with respect to single phase LSM (about one order of magnitude lower area specific resistance). In the case of mesoporous LSCF, a high-surface structure has been obtained by selectively etching a sacrificial phase from a starting biphasic VAN. The resulting final material exhibits a dramatically reduced activation energy for oxygen reduction reaction (as low as 0.4 eV), which is ascribed to combined microstructural and surface chemistry effects.

Such relevant findings are rationalized *via* a throughout investigation of the two systems, based on state-of-the-art structural (high-resolution transmission electron microscopy, atom probe tomography, low-energy ion scattering spectroscopy) and electrochemical (impedance spectroscopy) methods.

Layered Ceramic Protonic Electrolyzers Fabricated Via Inverse Tape Casting

*Kwati Leonard [AB] *, Mariya E. Ivanova [B], Wendelin Deibert [B], Wilhelm A. Meulenberg [B], Tatsumi Ishiraha [A], Hiroshige Matsumoto [A]*

[A] International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

[B] Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, Leo-Brandt-Str., D-52425 Jülich, Germany

Steam electrolysis *via* solid oxide electrolysis cell has been demonstrated to be a more efficient method to produce hydrogen using ceramics proton conducting electrolytes. These protonic solid oxide electrolysis cell (P-SOEC) devices can be successfully deployed to reach very high performance in hydrogen production. However, their fabrication techniques are still not yet quite rational at an industrial scale. Upscaling affordable large size (> 50 x 50 mm square) protonic devices meeting commercial targets is very challenging. The fabrication of such multilayered devices usually via a tape casting process requires careful control of shrinkages of individual layers to prevent warping, cracking during sintering.

This talk highlights the successfull processing of 5×5 cm^2 planar cathode-supported protonic electrolysis half-cell consisting of $Ba(Zr_{0.5}Ce_{0.4})_{8/9}Y_{0.2}O_{2.9}$ electrolytes, a functional NiO-$SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\delta}$ cathode layer and NiO-$Ba(Zr_{0.5}Ce0_{.4})_{8/9}Y_{0.2}O_{2.9}$ substrate using an inverse tape casting route. The smooth tri-layered green tapes produced, yielded suitably dense and gas-tight electrolyte layers after co-sintering at 1350 ºC/5h. Current-voltage characteristics and hydrogen evolution rates measured in the temperature range 500-600°C, using $Ba_{0.5}La_{0.5}CoO_{3-\delta}$ as anode, demonstrate excellent performance and durability. Electrolysis voltage as low as 1.2 V are attainable at current densities of 0.2, 0.4 and 0.5 A/cm^2 at 500, 550 and 600 ° C, achieving faradaic efficiencies close to 100% in the later, which is among the best PC-SOECs performance reported in literature. Microstructural optimized cells as well improvements in current collection also yield a current density of 1 Acm^2 at 600 ℃ at an operating voltage of 1.36 V. Beside electrochemical characteristics, the morphology of the tri-layered half-cells were also analyzed by a combination of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS). We observe the precipitation of Y_2O_3 and substential amount of Sr and Ba inter diffusion as well as Ni migrates in the vicinity of NiO grain and the electrolyte interface for all half-cells sintered at 1500 ºC.

This work was supported by the Cross-ministerial Strategic Innovation Promotion Program (SIP), “energy carrier”(Funding agency: JST), JSPS Core-to-Core Program of Advanced Research Networks (Solid Oxide Interfaces for Faster Ion Transport), the Ministry of Economy, Trade and Industry (METI), and by the International Institute for Carbon Neutral Energy Research (I2CNER) sponsored by the World Premier International Research Center Initiative (WPI), MEXT Japan.

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Hydration in BaLnLn’$Co_2O_{6-\sigma}$ cobaltites – a wide perspective.

Aleksandra Mielewczyk-Gryń 1), Ragnar Strandbakke 2), Sebastian Wachowski 1), Iga Szpunar 1), Ewa Dzik 1), Håkon Andersen 2), Maria Balaguer 3), Magnus H. Sørby 4), Jose M. Serra 3), Truls Norby 2), Maria Gazda 1)

1) Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland
2) Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway.
3) Instituto de Tecnología Química (Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas), Avenida de los Naranjos s/n.46022 Valencia, Spain
4) Department for Neutron Materials Characterization, Institute for Energy Technology, NO-2027 Kjeller, Norway

The cobaltites with perovskite-related structures are promising candidates for positrodes for SOFCs and SOECs. The general formula of investigated materials is BaLnLn’$Co_2O_{6-\delta}$ (Ln, Ln’ = La, Pr, Nd, Sm, Gd, Tb, Dy or Lu). In this system, different structures, starting from cubic (space group Pm-3m) to layered perovskites (e.g. space groups P4/m or Pmmm) can be adopted depending on the ionic radius of the lanthanide and the oxygen content. In some cases also superstructures may be formed.

In the last decade numerous oxides, that exhibit proton conductivity, have been introduced and extensively studied by multiple techniques unrevealing both transport properties and proton uptake thermodynamics. One of the most direct investigation methods designed to determine the latter is thermogravimetry (TGA). Two major types of study used to determine water uptake are switches from dry to humid atmosphere in the isobaric or the isothermal mode. In the case of barium lanthanide cobaltite, the isothermal approach proved to be suitable in contrary to isobaric approach. The quantification of the protonation level should take into consideration all possible processes that can be associated with water incorporation including hydration, hydrogenation, oxygenation and hydroxidation. In this work, the water uptake of multiple compositions from BaLnLn’Co_2O_6 system has been analyzed.

This work is a part of GoPHy MiCO project and authors would like to express their gratitude to M-era.Net consortium for support. The Polish contribution was supported by the European Commission and National Science Centre, Poland within M-era.Net initiative (project no 2016/22/Z/ST5/00691).