



"1st Electrochemical Society (ECS) Student Chapter Symposium"

Wednesday, 2nd of March, 2016

School of Chemistry University of St Andrews



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Programme:

Theatre D, School of Chemistry, St Andrews

Chairman: Iona Ross, PhD student and Treasurer of The ECS Student Chapter

1.30-1.40 pm

Opening Remarks

Irene Munaó, PhD Student and President of The ECS Student Chapter

1.40-1.55 pm

Talk: "NaFe₃(HPO₃)₂((H,F)PO₂OH)₆: a potential cathode material"

Irene Munaó, PhD student and President of The ECS Student Chapter

1.55-2.10 pm

Talk: "Determination of oxygen flux through dual phase oxygen transport membranes"

Zac Dehaney-Steven, PhD student and Vice-President of The ECS Student Chapter

2.10-2.25 pm

<u>Talk:</u> " $La_{0.20}Sr_{0.25}Ca_{0.45}TiO_3$ as a Solid Oxide Fuel Cell Anode 'Backbone' Material: Improving Performance through Microstructural Control"

Robert Price, PhD student and Secretary of The ECS Student Chapter

Common Room, School of Chemistry, St Andrews

Poster Session and Refreshment

2.30-3.30 pm

Poster session:

Redox-thermal stable Catalyst Oxide for Partial Oxidation	Amane Abdoun
Reforming POx	aa232@st-andrews.ac.uk
Donor Controlled Cation Aggregation in Magnesium Aluminates for Rechargeable Battery Electrolytes	Etienne Brouillet <u>e.brouillet@strath.ac.uk</u>
Impact of the annealing temperature on Pt/g-C ₃ N ₄ using EPR spectroscopy	Marine Caux <u>mc253@st-andrews.ac.uk</u>
Synthesis, structure and ionic conductivity of multiple aliovalent doping in ceria electrolytes	Alice V. Coles-Aldridge
	<u>aca4@st-andrews.ac.uk</u>
Rapid Oxygen Transport Membrane evaluation at St Andrews	Zac Dehaney-Steven
	<u>zads@st-andrews.ac.uk</u>
The identification and down selection of suitable cathode materials for use in next generation thermal batteries	Kyriakos. Giagloglou
	<u>kg53@st-andrews.ac.uk</u>
Solvothermal synthesis of some sodium – transition metal framework compounds for solid – state batteries	Irene Munaò <u>im49@st-andrews.ac.uk</u>
Improving the catalytic properties of the (La,Sr)(Cr,Fe,Ni)O₃ perovskite by in situ nanocatalyst exsolution	Despoina Papargyriou
	ap4&@st-andrews.ac.uk
La _{0.20} Sr _{0.25} Ca _{0.45} TiO ₃ as a Solid Oxide Fuel Cell Anode 'Backbone' Material: Improving Performance through Microstructural Control	Robert Price
	<u>rp63@st-andrews.ac.uk</u>
Copper Chromium Oxide Delafossites For Cathode Side Applications in SOFCs	Iona C. Ross
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Redox-thermal stable Catalyst Oxide for Partial Oxidation Reforming POx

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Several innovative and sustainable technologies have been investigated for producing, converting and storing energy, such as Solid Oxide Fuel Cells (SOFCs) for producing electricity thanks to hydrocarbon fuels, Solid Oxide Electrolyser Cells (SOECs) for producing hydrogen or syngas thanks to steam or steam and CO₂ respectively. Currently, SOFC have been mainly carried out using a Ni-YSZ cermet as fuel electrode with an oxygen anion conducting electrolyte. However, because of the deactivation of Ni (Ni coarsening) and the deposition of carbon, under hydrocarbon or CO_2/CO mixture atmospheres, issues on the performance have been highlighted.¹ Hence, due to its multifunctional performance, the Electrochemical Membrane Reactor (EMR) has drawn all the attention as one which allows the combination of H₂O steam electrolysis and the synthesis of syngas based on the reduction of CH₄ and CO₂.² Therefore, we will investigate new ideal electrode material, which should have high electrical conductivity and electro-catalytic activity as well as high resistance against coking and to sulphur contaminants. Therefore, $Ce_{1-x}Cu_xO_{2-\delta}$ has a fluorite structure (Space Group Fm-3m) and can retain its structure when releasing (or incorporating) oxygen. That's why, because of its interesting properties, which are linked to its Oxygen Storage Capacity³, $Ce_{1-x}Cu_xO_{2-\delta}$ is a promising candidate as a metal oxide electrode. This work shows the initial research into the behavior of $Ce_{1-x}Cu_xO_{2-\delta}$ in order to get a better comprehension of its surface properties and also to inquire about its electrochemical properties by infiltration method on La(Sr)Cr(Mn).



Fig. 1 Functioning Principle of the EMR

- 1. E. P. Murray, T. Tsai and S. A. Barnett, *Nature*, **1999**, 400, 649.
- 2. C. Graves, S. D. Ebbesen, S. H. Jensen, S. B. Simonsen and M. B. Mogensen, Nat Mater, 2015, 14, 239.
- 3. X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias and M. Fernández-García, *The Journal of Physical Chemistry B*, **2005**, 110, 428.

Donor Controlled Cation Aggregation in Magnesium Aluminates for Rechargeable Battery Electrolytes

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Magnesium is currently receiving widespread attention as a potential replacement for lithium in the field of rechargeable batteries, due in part to its greater natural abundance (and hence lower cost), its higher volumetric capacity and its high reduction potential. Unfortunately, simple binary Mg salts present unsurmountable problems, however a magnesium aluminate modification shows considerable promise as electrolytic material. The cationic magnesium moiety of these magnesium organohaloaluminates typically takes the thermodynamically favourable dinuclear $[Mg_2Cl_3]^+$ form in the solid-state although other oligomeric forms have been proposed to participate. Our studies have revealed that judicious choice of Lewis donor allows the deliberate synthesis and isolation of these postulated mononuclear $[MgCl]^+$ and trinuclear $[Mg_3Cl_5]^+$ modifications, forming a comparable series with a common aluminate anion $[(Dipp)(Me_3Si)NAlCl_3]^-$ suitable for probing the effect of cation oligomerization on performance. By pre-forming the Al-N bond prior to introduction of the Mg source, a consistently reproducible protocol has been obtained. Solution state analysis by NMR spectroscopy and Electrospray Ionisation Mass Spectrometry (ESI-MS) has been utilized to study the equilibrium processes between the different aggregation states.



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2. H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour and D. Aurbach, *Energy Environ. Sci.*, **2013**, 6, 2265.

3. T. Liu, J. T. Cox, D. Hu, X. Deng, J. Hu, M. Y. Hu, J. Xiao, Y. Shao, K. Tang and J. Liu, *Chem. Commun.*, **2015**, 51, 2312.

Impact of the annealing temperature on Pt/g-C₃N₄ using EPR spectroscopy

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Photo-catalytic hydrogen production from water or from organic wastes is an important aspect in securing a sustainable economy relying on solar energy for future technologies. Many generations of photo-catalysts have been made and studied since the pioneering work of Fujishima and Honda¹. Among the materials of recent interest are those based on $g-C_3N_4$ due to their stability and relatively small band gap (2.7 eV)² when compared to other stable wide band gap materials. In this work we investigate the effect of temperature during the synthesis of $g-C_3N_4$ from melamine on the catalyst activity for hydrogen production, using oxalic acid as a sacrificial agent. This is combined with an electron paramagnetic resonance study and CHN analysis. Synthesis temperature affects the extent of the 2D ordering within polymer and therefore is poised to have an effect on the paramagnetic species concentration. EPR data performed on $g-C_3N_4$ (synthetized at 500°C) shows a single Lorentzian line with a g value between 2.0041 and 2.0051 in agreement with previous studies ^{3,4}. Loading the photo-catalyst with 1 wt% platinum has shown a slight increase of the EPR signal compared to the bare sample; this is in contrast with what has been observed by Bruckner *et al.* ³. We suggest that the highly delocalized system results in a superposition of the electron and hole signals, having similar g values.



Fig.1 EPR signals in the dark and under 400nm light irradiation (450W) of bare g-C₃N₄ and reduced Pt/g-C₃N₄

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4. D. Rovnyak, M. Baldus, B. a Itin, M. Bennati, a Stevens, and R. G. Griffin, J. Phys. Chem. B, 2000, 104, 9817.

Synthesis, structure and ionic conductivity of multiple aliovalent doping in ceria electrolytes

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Owing to their high oxygen ion conductivity, aliovalently doped ceria electrolyte materials are of great interest for use in solid oxide fuel cells and oxygen sensors. The accepted strategy for improving ionic conductivity involves doping these materials with trivalent lanthanide elements such as Gd³⁺ and Sm³⁺. These substitutions, as well as the processing conditions of the final electrolyte materials, influence total conductivity via both microstructure-dependent grain boundary and intrinsic bulk effects. In this study, the effects of aliovalent doping with one, two and more lanthanide elements on these microstructural and intrinsic factors are investigated by preparing and evaluating a series of singly, doubly and triply-substituted ceria electrolytes.

A citrate-nitrate complexation method was used to produce these singly, doubly and triply-doped cerias containing varying amounts of Gd, Sm and Nd. This method results in very pure and fine oxide powders.¹ XRD and TEM were used to determine the crystallography of these materials. The powders were sintered under a standard set of conditions to produce dense ceramic electrolytes for comparison. Impedance spectroscopy was employed to obtain oxygen ion conductivity data at a wide range of temperatures. Both intrinsic and grain boundary conductivity were followed. The effect of grain structure– determined by SEM– on conductivity was determined. A number of other supporting measurements were also performed to confirm the crystal structure and chemical compositions.

The results will be discussed in terms of the advantage or otherwise over the singly-doped materials of combining two and three dopants.

Rapid Oxygen Transport Membrane evaluation at St Andrews

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Oxygen transport membranes show promise s a replacement for cryogenic oxygen separation in the fields of oxyfuel combustion for CCS, production of syngas and lab-scale oxygen production. The causes and mechanisms of degradation are not fully understood, and there is potential to improve oxygen flux. Real-world systems are large and tubular, making evaluation of new materials expensive and difficult. Small planar architecture suits this rapid-screening process better, as cells are easier, quicker and cheaper to fabricate.

Oxygen transport membranes of the type being evaluated in the present study comprise a porous support layer, fuel oxidation layer, dual phase (ionic and MIEC) dense layer and an oxygen reduction layer.

The dense layer's composition of an ionically conductive phase and a mixed ionic electronic conductor allows flow of electrons in the opposite direction to the oxide ion migration to maintain charge neutrality. Because no current is drawn (in contrast to SOFC) the driving force is chemical potential.

This study is primarily concerned with developing test capability for the rapid screening of cell assemblies, and understanding the causes and mechanisms of degradation in the fuel oxidation layer and dense layer.



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2. W. Fang, Y. Zhang, J. Gao, C. Chen, Ceram. Int., 2014,40, 799.

3. Wagner, C, Prog. Solid State Chem., 1975, 10(1), 3.

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The identification and down selection of suitable cathode materials for use in next generation thermal batteries

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Thermal batteries are electrochemical systems that convert chemical energy into electrical energy by means of an electrochemical oxidation-reduction reaction between the anode and the cathode electrode. These batteries are able to provide higher energy conversion efficiencies than common batteries and find usage in critical systems where high reliability is crucial. They are known for their ability to be stored for long periods of time (> 25 years), their ability to be started rapidly (< 1 s) and their ability to be discharged at extremely high rates compared to standard batteries¹. Moreover, thermal batteries supply power to ejector seats, guided munitions and emergency power systems on aircraft. Thermal batteries are composed of a number of individual electrochemical cells that have three key components: a cathode, an anode, and an electrolyte. In this case the thermal prefix is related to the electrolyte, a halide salt eutectic that is only ionically conductive when molten (>350°C). Contemporary cells often use a lithium alloy as the anode, a halide salt eutectic bound in an insulating porous material as the electrolyte, and a transition metal sulfide as the cathode. These transition metal disulfides such as FeS₂, NiS₂ and CoS₂ are very common and all of these materials can supply voltages of ~ 1.7 V vs. $Li_{13}Si_4^{2,3}$. ZrS₃, CoNi₂S₄, Li_6VCl_8 and KNiCl₃were synthesized by solid state reaction. At a high temperature of 500°C and 425°C the value of the working voltage plateau recorded for different values of constant current. (Fig.1)



Fig.1 XRD pattern of CoNi₂S₄

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Solvothermal synthesis of some new 3-D sodium transition metal framework compounds for solid – state batteries

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In the last few years, two concepts have become key issues in daily life: energy conversion and energy storage. Recently the demand for large scale batteries to store the electricity in a renewable and cleaner way has become important in the energy problem. Batteries are the best way to store chemical energy and to deliver it as electrical energy. In the last decades an interest about low-cost, safe and rechargeable batteries with adequate properties (voltage, capacity, rate capability) has increased. Since they were discovered¹, the best candidates for this role have been Li-ion batteries, which became the fundamental energy source for all portable electronic devices². However the increasing cost of lithium, questions over its future availability, together with health and safety problems mean that, in the last few years, research for new materials to substitute lithium has started. The best candidate is found in sodium. In contrast to lithium, sodium is cheap and unlimited and also, from the chemistry point of view, it is the second lightest and smallest alkali metal next to lithium. Hence, rechargeable sodium ion batteries could be the promising candidates for a lot of applications³. Due to the low cost, the availability and the abundance of sodium, the interest in the synthesis of electrodes based on sodium has increased, especially using solvothermal methods. In this poster we present two aspects of our work. First, a novel perovskite, Na₂MoO_{2- δ}F_{4+ δ} (δ ~ 0.08), which exhibits some unique structural features, and also has potential as an intercalation host.⁴ Second, a novel iron phosphite, NaFe₃(HPO₃)₂((H,F)PO₂OH)₆ which shows reversible intercalation of Na⁺ ions, with an average discharge voltage of 2.5 V and an experimental capacity of up to 90 mAh/g.⁵



Fig.1 Polyhedral view of $Na_2MOO_{2-\delta}F_{4+\delta}$ and $NaFe_3(HPO_3)_2((H,F)PO_2OH)_6$

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Improving the catalytic properties of the (La,Sr)(Cr,Fe,Ni)O₃ perovskite by in situ nanocatalyst exsolution

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In the present study the (La,Sr)(Cr,Fe,Ni)O₃ perovskite was synthesized and characterized for the fuel oxidation layer of Oxygen Transport Membranes. The catalytic properties of the perovskite were improved by the incorporation of a catalyst with the method of in situ nanocatalyst exsolution, which tends to grow pinned metal nanoparticles on the reduced oxide surface.¹

 $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_3$ (LSCF) perovskite with partial substitution of the B site by 5 mol% of Ni was synthesized via a modified Pechini method. X-ray diffraction showed that LSCF exhibits an orthorhombic structure and after doping the B site with 5mol% of Ni the perovskite is retaining its structure with a small decrease on the unit cell parameters. The formation of exsolved nanoparticles (30-50 nm) on the LSCFNi surface was observed by SEM, after reducing the samples in 5%H₂/Ar at 900°C. TEM-EDX analysis of these nanoparticles indicated that their composition is an Fe-Ni alloy. The exsolution of the nanoparticles can be controlled by changing the reduction conditions and the B site dopant. Catalytic testing of the LSCF and LSCFNi was conducted at 900oC with a standard gas composition of CH₄, CO₂ and H₂. LSCFNi showed a 22.5% CH₄ conversion, which was 5 times higher than LSCF, confirming the catalytic activity of the exsolved nanoparticles.

La_{0.20}Sr_{0.25}Ca_{0.45}TiO₃ as a Solid Oxide Fuel Cell Anode 'Backbone' Material: Improving Performance through Microstructural Control

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In order to overcome the shortfalls of the Ni-based cermet as a solid oxide fuel cell (SOFC) anode material, mixed ionic and electronic conductor (MIEC) materials are being researched as potential alternatives ¹. A MIEC can be produced by taking an oxide 'backbone' material and impregnating it with electrocatalytically active transition/lanthanide metals/metal oxides. These materials have the potential to exhibit higher redox stability, sulphur and coking tolerance (in the presence of a hydrocarbon fuel gas) and reduced catalyst particle agglomeration ¹.

The A-site deficient perovskite: $La_{0.20}Sr_{0.25}Ca_{0.45}TiO_3$ (LSCT_{A-}) has previously been employed as a solid oxide fuel cell anode 'backbone' material on an industrially relevant scale at Hexis AG, Switzerland. Employment of a NiO and $Ce_{0.80}Gd_{0.20}O_{1.9}$ impregnated LSCT_{A-} anode in the Hexis Galileo 1000 N micro-combined heat and power unit (60 cell stack – 1 kW) initially showed a promising power output of 700 W. Unfortunately, this performance degraded to ~250 W after 600 hours of operation and this was attributed to very thin, dense anode microstructures (leading to poor current distribution), as well as the agglomeration of the Ni electrocatalyst particles².

Due to the promising performance demonstrated, further research is now taking place on this material. In this work, ceramic processing techniques have been used as the primary method in controlling anode 'backbone' microstructure. An explanation of the rheological properties of LSCT_A- inks (for screen printing), their interaction with screens of differing mesh count and the importance of the sintering protocol employed will be presented. Also, conductivity data for a series of microstructural architectures will be presented along with some simple models used to predict the required thickness of the anode layer to ensure good lateral conductivity and current collection.

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^{2.} Verbraeken, M. C. et al., 11th European SOFC and SOE Forum, **2014**, 1.

Copper Chromium Oxide Delafossites For Cathode Side Applications in SOFCs

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Issues such as element sustainability, cost and durability are important concerns for materials at the cathode side of the solid oxide fuel cell1 (SOFC). Compositions which could provide a barrier material from the chromium rich steel interconnects while also being composed of high abundance elements, or with a lower volume of expensive rare earth elements, would be of interest. Delafossite type structures (A¹⁺B³⁺O₂) have applications as optoelectronic transparent p-type conducting oxides2, and as thermoelectrics3 devices. Delafossite copper chromium oxide, alongside compositions doped with magnesium (CuCr_{1-x}Mg_xO₂, x=0.05-0.3), were investigated to observe their suitability for cathode side applications in SOFCs. The compositions were found to be stable from room temperature to 800°C in air, with thermal expansion coefficients ranging from 7.5 – 10.8 $\times 10^{-6}$ K⁻¹. X-ray diffraction (XRD) and scanning electron microscopy showed that the larger Mg dopant volumes introduced a secondary spinel phase (MgCr2O4) as ~0.5µm octahedral particles embedded in the delafossite surface. The conductivities of the samples were found to be between 1– 15 S cm⁻¹ at 800°C for 50% dense compositions, with CuCr_{0.975}Mg_{0.025}O₂ displaying the highest conductivity. Doped samples were intimately mixed with conventional electrolyte materials yttria stabilized zirconia (YSZ) and gadolinium doped ceria (GDC) before being annealed at 800°C for 10 hours in air. XRD analysis of the resulting mixtures showed a peak at 28.3° 20 in the delafossite-YSZ pattern that might be attributed to the strongest reflection of CuZrO3. No new phase formation was seen for the delafossite-GDC XRD patterns. Research was funded by the EPSRC and H2FC Supergen Hub.



Fig.1 Scanning electron microscopy image of the surface of $CuCr_{0.99}Mg_{0.01}O_2$ with octahedral particles of the secondary phase $MgCr_2O_4$

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