THE POWER OF INTERFACES 2022

PROGRAM AT A GLANCE

Venue: Palma CaixaForum (Plaza de Weyler, 3. 07001 Palma)

	Wednesday, Oct 5th		**Thursday, Oct 6th**	**Friday, Oct 7th**
	Meetings	School	Workshop	Workshop
	Room: Espai D	Room: Georges Bernanos	Room: Lluís Domènech i Muntaner auditory	Room: Lluís Domènech i Muntaner auditory
	Floor 2	Floor 3	Floor -1	Floor -1
			Registration and opening	
9:00	Registration Opening		9:00-10:35 Session 1 - Advanced techniques	9:00-10:50 Session 5 - Modelling
10:00	10:00 - 13:30 Harvestore meeting	10:00 - 12:00 Fundamentals		
			Coffee-break	
11:00			11:00-12:50 Session 2 - Devices	Coffee-break
				11:15-13:00 Session 6 - Protonics
12:00		12:00-13:00 Devices I		
13:00		Lunch	Lunch	Lunch
14:00	Lunch			
		14:30-16:30 Devices II	14:30-15:35 Session 3 - New materials	14:30-16:05 Session 7 - Heterostructures
15:00	15:00-18:30 Epistore meeting		Break	
16:00		Break	16:00-17:30 Session 4 - Interfaces and surfaces	Closing ceremony and awards
17:00		16:45-18:45 Advanced techniques		
			17:30-19:00 Poster session (Espai D)	
18:00				
19:00	19:00-22:00 Welcome reception for all the participants			
20:00				
21:00			21:00 Social gathering	
22:00				

Organisers

DAY ONE

5th of October

Project meeting and School

Registration starts at 9:30 - In front of Room George Bernanos (Floor 3)

PoI22 SCHOOL

Room George Bernanos (Floor 3)

	9:45	Opening	
	10:00	Fundamentals of defect chemistry	Ainara Aguadero
Fundamentals	11:00	Bulk ion transport	Stephen Skinner
	12:00	Fundamentals of solid state batteries	Louis De Taeye
	13:00	Lunch*	
	14:30	Thermodynamics and kinetics of SOCs	Juergen Fleig
Devices	15:30	SOC technologies	Miguel Laguna
	16:30	Break	
Advanced techniques	16:45	Ion beam techniques	John Kilner
	17:45	Impedance spectroscopy	Dino Klotz

*Wednesday’s lunch is not provided

PROJECT MEETINGS (for project members only)

Room Espai D (Floor 2)

10:00 – 13:30	Harvestore project meeting
13:30 – 15:00	Lunch*
15:00 – 18:30	Epistore project meeting

*Wednesday’s lunch is not provided

WELCOME RECEPTION

Welcome reception for all the PoI22 participants

19:00

Adalt Brewing
C/ de l'Arxiduc Lluís Salvador, 40, 07004 Palma
www.adaltbrewing.com

DAY TWO

6th of October

Power of Interfaces workshop

Registration starts at 8:30 – In front of Room Lluís Domènech i Muntaner (Floor -1)

POWER OF INTERFACES WORKSHOP

Room Lluís Domènech i Muntaner (Floor -1)

8:45		Opening	
Session 1 - Advanced techniques (chair: Zijie Sha)			
9:00	K	Nicola Perry	Shining light on defect kinetics in mixed conducting oxide thin films
9:30	I	Monica Burriel	Original in situ Raman spectroscopy approaches to characterise solid oxide cell electrodes and electrolytes
9:50	C	Giulio Cordaro	High-Throughput Investigation of Combinatorial Thin Film Ternary System as Electrolytes for Protonic Ceramic Cells
10:05	C	Francesco Chiabrera	Defect Chemistry of Lanthanum Ferrite Thin Films during Ion Intercalation in alkaline electrolytes
10:20	C	Juande Sirvent	High-throughput methodologies for the study of cathodes in solid oxide cells: the $La_{0.8}Sr_{0.2}Co_xMn_yFe_{1-x-y}O_3$ perovskite family
10:35		Coffee-break	
Session 2 – Devices (chair: Aleksandra Mielewczyk-Gryń)			
11:00	K	Magda Titirici	Beyond Li-ion batteries: performance, materials diversification, and sustainability
11:30	K	Miguel Laguna	Novel architecture designs for solid state energy devices by laser machining
12:00	I	Marta Fernández	Micro and nanotechnologies for autonomous energy devices
12:20	C	Alexander Schmid	Rechargeable oxide ion batteries based on mixed conducting intercalation electrodes
12:35	C	Sonia Escolástico	Direct electrocatalytic CO_2 reduction in a tubular protonic membrane reactor
12:50		Lunch (at Caixaforum restaurant)	
Session 3 - New materials (chair: Hiroshige Matsumoto)			
14:30	I	Miriam Botros	High-Entropy materials for energy applications
14:50	C	Fjorelo Buzi	A Cobalt-based nanocomposite for increased electrochemical stability at high temperature in Solid Oxide Fuel Cell
15:05	C	Tatsumi Ishihara	Bismuth niobium oxychloride, Bi_4NbO_8Cl, as a New Layered Oxide Ion Conductor
15:20	C	Wenrui Zhang	New Oxide-ion Conductors of the Dion–Jacobson phases $CsM_2Ti_2NbO_{10-\delta}$ (M = Bi, La)
15:35		Break	
Session 4 - Interfaces and surfaces (chair: Laura Almar)			
16:00	I	John Irvine	Nanoengineering of Electrochemical interfaces
16:20	C	Zijie Sha	The effect of operating environments on surface composition evolution of perovskite-type mixed conducting electrodes
16:35	C	Filippo Colombo	Bimetallic exsolution from perovskite oxides: an insight on mechanistic aspects through in-situ measurements for tailoring catalytic selectivity
16:50	C	Alfonso Carrillo	Tuning ternary alloyed nanoparticle composition by exsolution
17:05	C	Matthew Wells	Towards High-Performance, Low-Temperature Solid Oxide Cells with Vertically Aligned Nanocomposite Films
17:30 – 19:00		Poster session (Espai D, Floor 2) – Check extended program	

K: keynote I: invited talk C: contribution

SOCIAL GATHERING

21:00	Social gathering	A social meeting point will be proposed during the opening session

DAY THREE

7th of October

Power of Interfaces workshop

POWER OF INTERFACES WORKSHOP			
Room Lluís Domènech i Muntaner (Floor -1)			
Session 5 – Modeling (chair: Francesco Chiabrera)			
9:00	K	Alexander Opitz	Geometrically well-defined model systems as a powerful tool for a deeper understanding of electrochemical elementary processes in solid oxide cell research
9:30	I	Aleksandar Staykov	Oxygen activation and dissociation on transition metal free complex oxide surfaces. Insights from the theory
9:50	C	Kulbir Ghuman	Modeling Defects in Polycrystalline Materials
10:05	C	Dennis Kemp	Recipes for superior ionic conductivities in thin-film ceria-based electrolytes
10:20	C	Jose Carlos Madrid	Molecular Dynamics Study of Oxygen-Ion Diffusion in Yttria-Stabilized Zirconia Grain Boundaries
10:35	C	Silvère Panisset	A 3D Finite Element Method model designed for nanocolumnar µSOC oxygen electrodes
10:50		Coffee-break	
Session 6 – Protonics (chair: Albert Tarancon)			
11:15	K	Sossina Haile	Proton Transfer Kinetics at Interfaces with the Superprotonic Electrolyte CsH_2PO_4
11:45	K	Hiroshige Matsumoto	Insertion of electron-blocking layer at steam/air electrode for suppression of electronic leakage in proton-conductor cells
12:15	C	María Balaguer	Evaluation of the stability of PCFC electrodes based on double perovskite cobaltites
12:30	C	Aleksandra Mielewczyk-Gryń	Influence of stochiometric complexity on performance of multi-constituent ceramic protonic conductors
12:45	C	Laura Almar	Redox-stable electrodes for CH_4 conversion in proton ceramic cells
13:00		Lunch (at Caixaforum restaurant)	
Session7 – Heterostructures (chair: Kulbir Ghuman)			
14:30	K	Dino Klotz	Grain Boundaries under Light – What is happening
15:00	C	Kosova Kreka	Towards better oxygen electrodes for r-µSOC: Investigation of LSC and LSM based VAN electrodes under bias.
15:15	C	Alexander Stangl	Enhancing SOC cathode performance using tailored nano-columnar La2NiO4+δ thin films
15:30	I	Daniele Pergolesi	Photocatalytic water splitting with oxynitride semiconductors: in situ and operando characterizations of the solid-liquid interface
15:50	C	Anton Kaus	Hybrid oxide superlattices as electrocatalysts for the oxygen evolution reaction in alkaline electrolyte
16:05			Closing ceremony and prizes

K: keynote I: invited talk C: contribution

POSTER SESSION

DAY TWO – Thursday, 6th of October (17:30-19:00)
Room: Espai D

Poster contributions

Alexander Bonkowski	A molecular-dynamics study of oxygen diffusion in polycrystalline (La,Sr)FeO_3
Apostolos Panagiotopoulos	State-of-the-art surface analysis via simultaneous positive and negative ion detection
Jingdong Xu	Interface characterization of exposed lanthanum strontium chromium ferrite air electrode
Adeel Riaz	$La_2NiO_{4+\delta}$ Electrodes by Pulsed-Injection MOCVD: Deposition Strategies and Microstructural Characterization
Jair Gabriel Triana-Pequeño	Exsolved nanoparticles from doped $LaAlO_3$ perovskite: towards lowering the exsolution temperature
Rosalía Cid Barreno	XPS insight on the improved polymer electrolyte–Li metal interface on high-voltage solid-state batteries driven by additives
Lorenzo Fallarino	Building 3D metal anode for Lithium-Ion Batteries
Jan Speulmanns	Interfacial challenges in 3D thin-film Li-ion batteries by atomic layer deposition
Yuta Yasui	Oxide-ion conductivity and structural disorder of hexagonal perovskites $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ and $Ba_3MNbO_{8.5}$ (M = Mo, Nb)
Claudia Steinbach	Investigating the space charge at mixed ionic and electronic conducting oxide heterojunctions
Carmen de la Torre Gamarra	Scalable manufacturing of electrode-supported planar solid oxide electrolizer cells (SOECs)
Philip Klein	Investigation and feasibility study of $SrTiO_3$ thin films in high – temperature solid oxide solar cells
Alexander Schmid	High-pressure oxygen in closed pores of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ electrodes
Riho Morikawa	New hexagonal perovskite-related oxides exhibiting high proton conductivity
Francesco Chiabrera	The impact of antisite defects on the oxygen mass transport properties of $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ thin films
Imran Ashgar	Additive manufacturing of ceramic nanocomposite fuel cells
Princess Inangha	Visualizing exsolved nanoparticles by anomalous X-Ray scattering methods
George Harrington	The role of above band-gap radiation on ionic transport at grain-boundaries in Gd-substituted ceria from impedance and tracer diffusion studies
Arindom Chatterjee	Infrared thermography for thermal transport properties

KEYNOTES, INVITED TALKS AND ORAL CONTRIBUTIONS

DAY TWO AND THREE - 6th and 7th of October
Room Lluís Domènech i Muntaner

Keynotes and invited talks

K	**Nicola Perry**	Shining light on defect kinetics in mixed conducting oxide thin films
K	**Magda Titirici**	Beyond Li-ion batteries: performance, materials diversification, and sustainability
K	**Miguel Laguna**	Novel architecture designs for solid state energy devices by laser machining
K	**Alexander Opitz**	Geometrically well-defined model systems as a powerful tool for a deeper understanding of electrochemical elementary processes in solid oxide cell
K	**Sossina Haile**	Proton Transfer Kinetics at Interfaces with the Superprotonic Electrolyte CsH_2PO_4
K	**Hiroshige Matsumoto**	Insertion of electron-blocking layer at steam/air electrode for suppression of electronic leakage in proton-conductor cells
K	**Dino Klotz**	Grain Boundaries under Light – What is happening
I	**Monica Burriel**	Original in situ Raman spectroscopy approaches to characterise solid oxide cell electrodes and electrolytes
I	**Marta Fernández**	Micro and nanotechnologies for autonomous energy devices
I	**Miriam Botros**	High-Entropy materials for energy applications
I	**John Irvine**	Nanoengineering of Electrochemical interfaces
I	**Aleksandar Staykov**	Oxygen activation and dissociation on transition metal free complex oxide surfaces. Insights from the theory
I	**Daniele Pergolesi**	Photocatalytic water splitting with oxynitride semiconductors: in situ and operando characterizations of the solid-liquid interface
C	**Giulio Cordaro**	High-Throughput Investigation of Combinatorial Thin Film Ternary System as Electrolytes for Protonic Ceramic Cells
C	**Francesco Chiabrera**	Defect Chemistry of Lanthanum Ferrite Thin Films during Ion Intercalation in alkaline electrolytes
C	**Juande Sirvent**	High-throughput methodologies for the study of cathodes in solid oxide cells: the $La_{0.8}Sr_{0.2}Co_xMn_yFe_{1-x-y}O_3$ perovskite family
C	**Alexander Schmid**	Rechargeable oxide ion batteries based on mixed conducting intercalation electrodes
C	**Sonia Escolástico**	Direct electrocatalytic CO_2 reduction in a tubular protonic membrane reactor
C	**Fjorelo Buzi**	A Cobalt-based nanocomposite for increased electrochemical stability at high temperature in Solid Oxide Fuel Cell
C	**Tatsumi Ishihara**	Bismuth niobium oxychloride, Bi_4NbO_8Cl, as a New Layered Oxide Ion Conductor
C	**Wenrui Zhang**	New Oxide-ion Conductors of the Dion–Jacobson phases $CsM_2Ti_2NbO_{10-\delta}$ (M = Bi, La)
C	**Zijie Sha**	The effect of operating environments on surface composition evolution of perovskite-type mixed conducting electrodes
C	**Filippo Colombo**	Bimetallic exsolution from perovskite oxides: an insight on mechanistic aspects through in-situ measurements for tailoring catalytic selectivity
C	**Alfonso Carrillo**	Tuning ternary alloyed nanoparticle composition by exsolution
C	**Matthew Wells**	Towards High-Performance, Low-Temperature Solid Oxide Cells with Vertically Aligned Nanocomposite Films
C	**Kulbir Ghuman**	Modeling Defects in Polycrystalline Materials

Keynotes and invited talks

C	**Dennis Kemp**	Recipes for superior ionic conductivities in thin-film ceria-based electrolytes
C	**Jose Carlos Madrid**	Molecular Dynamics Study of Oxygen-Ion Diffusion in Yttria-Stabilized Zirconia Grain Boundaries
C	**Silvère Panisset**	A 3D Finite Element Method model designed for nanocolumnar µSOC oxygen electrodes
C	**María Balaguer**	Evaluation of the stability of PCFC electrodes based on double perovskite cobaltites
C	**Aleksandra Mielewczyk-Gryń**	Influence of stochiometric complexity on performance of multi-constituent ceramic protonic conductors
C	**Laura Almar**	Redox-stable electrodes for CH_4 conversion in proton ceramic cells
C	**Kosova Kreka**	Towards better oxygen electrodes for r-µSOC: Investigation of LSC and LSM based VAN electrodes under bias.
C	**Alexander Stangl**	Enhancing SOC cathode performance using tailored nano-columnar $La_2NiO_{4+\delta}$ thin films
C	**Anton Kaus**	Hybrid oxide superlattices as electrocatalysts for the oxygen evolution reaction in alkaline electrolyte

A molecular-dynamics study of oxygen diffusion in polycrystalline $\mathrm{(La,Sr)FeO_3}$

A. Bonkowski[1], J. A. Kilner[2], R. A. De Souza[1]

[1]Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany.

[2]Faculty of Engineering, Department of Materials, Imperial College London, London, UK.

$\mathrm{(La,Sr)FeO_3}$ is a well-known mixed ionic and electronic conducting perovskite oxide [1-5], with application in Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs).

In this study we employed molecular-dynamics (MD) simulations based on empirical force fields [6,7] to investigate oxygen transport in the solid solution $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_{3-x/2}$ (x = 0.1, 0.25 and 0.4). Simulations were performed at temperatures $1000 \leq T\,/\,\mathrm{K} \leq 3000$. Oxygen tracer diffusion coefficients obtained for both orthorhombic and cubic structures are compared with experimental data [1-5], and are found to give a satisfactory description of the oxygen transport behaviour as a function of T and x. Subsequently, we examined oxygen tracer diffusion in polycrystalline cells of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_{3-x/2}$ with differing numbers of grain boundaries. In all cases, we find that oxygen tracer diffusion in the polycrystalline systems is lower than in the single-crystal systems. Our results thus indicate that in perovskite-oxide ceramics with homogeneous cation distributions there is no faster diffusion of oxygen along grain boundaries. A detailed analysis of diffusion data for polycrystalline simulation cells is demonstrated with a new in-house analysis tool [8].

[1] T. Ishigaki, S. Yamauchi, K. Kishio, J. Mizusaki, K. Fueki, J. Solid State Chem. ***1988****, 73, 179–187.*

[2] J. E. ten Elshof, M. H. R. Lankhorst, H. J. M. Bouwmeester, J. Electrochem. Soc. ***1997****, 144, 1060–1067.*

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[7] M. S. Islam, M. Cherry, C. R. A. Catlow, J. Solid State Chem. ***1996****, 124, 230–237.*

[8] https://github.com/ab5424/agility.

State-of-the-art surface analysis via simultaneous positive and negative ion detection.

Apostolos Panagiotopoulos[1], Nomaan Nabi[1], George E. Wilson[1], Sarah Fearn[1], Richard Chater[1], Stephen Skinner[1], John Kilner[1] and Ainara Aguadero[1,2]

[1]Department of Materials, Imperial College London, UK

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Surface and bulk processes of electronic and electrochemical devices have been studied extensively yet they are poorly understood. This work aims to provide a holistic observation of electronic interactions within the solid-state of the electronic conductor(electrode) and into the ionic conductor(electrolyte), through combined ion^{+-} beams. Specifically, a bespoke ultra-high-vacuum mass spectrometer is employed to simultaneously collect and align positive and negative ion images.

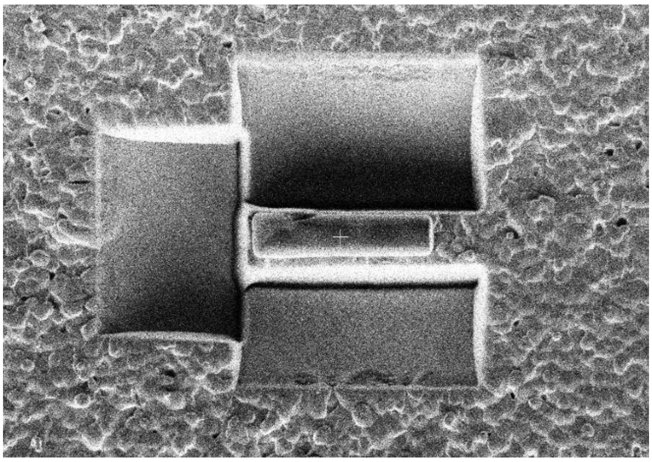
Combining a plasma-FIB with Pt sputtering capabilities, we demonstrate complete elemental and ionic 3D depth profiling of topographic features and study how these evolve *in-operando*. For the first time, we can trace charge transport, ion diffusion and interfacial electrochemical interactions in sub-micron particles, nano-scale grain boundaries for a plethora of electronic and electrochemical devices with ppm accuracy.

Interface characterization of exposed lanthanum strontium chromium ferrite air electrode

Jingdong Xu

Imperial College London

Energy consumption has been increasing over past decades. The use of electricity, as the typical form of energy structure, is estimated to be doubled by 2050. High demand of electricity poses significant challenges in energy supply. Currently, production of electricity remains highly dependent on combustion of fossil fuel. Limited by thermodynamic restrictions, the efficiency of thermal power is relatively low and results in deteriorated greenhouse emission and pollution. Fuel cell thus becomes a promising area to build a clean energy future, since it directly converts fuel into electricity. Working at high temperature, solid oxide fuel cell (SOFC) is a competitive candidate, which exhibits attractive reactivity and efficiency in energy transformation. However, SOFC devices that work for long period encounter performance penalty and reduced stability. The mechanism of the degradation is unclear, and it is believed that change of microstructure can be the critical reason. Different from research of oxygen migration using isotope exchange, study of cation is challenging. In this research, air electrode material of lanthanum strontium chromium ferrite (LSCrF) was exposed under various temperature and time to characterize the evolution of cation. Chemical composition of air-solid interface was investigated by X-ray photoelectron spectroscopy (XPS). Deconvolution of XPS spectra revealed iron and strontium was significantly aggregated to the interface. Iron and strontium however showed different trends, with nearly doubled strontium found in the top layer and approximately 30% increased for iron. Depth profile of cation distribution was analyzed using secondary ion mass spectrometry (SIMS). FeO- and SrO- were detected and significantly enriched on the interface compared to LSCrF bulk. In order to directly characterize the migration of cation, focused ion beam – scanning electron microscopy (FIB-SEM) was conducted to construct a cross-section sample. The microstructure in SEM displayed a dense section with small proportion of pores and defects. The cross-section sample was then thinned to be compatible with scanning transmission electron microscopy (STEM). The chemical distribution of sample was evaluated by energy dispersive x-ray spectroscopy (STEM-EDS). Line profiling of the cross-section sample exhibited enhanced intensity of strontium and iron on the solid-air interface, with a good agreement with SIMS result. Some depletion structure of iron was also observed, with approximately 5% lower concentration compared to the bulk.



$La_2NiO_{4+\delta}$ Electrodes by Pulsed-Injection MOCVD: Deposition Strategies and Microstructural Characterization

Adeel Riaz[1], Alexander Stangl[1], Laetitia Rapenne[1], Silvère Panisset[1], Carmen Jiménez[1], Michel Mermoux[2] and Mónica Burriel[1]

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$La_2NiO_{4+\delta}$ is a promising electrode material for low temperature reversible-solid oxide cells (r-SOC) due to its good electronic and ionic conductivity, high oxygen exchange activity and a low activation energy. Thin films are limited by the surface reaction, hence, optimizing the nanostructure can lead to enhanced electrode performance. Pulsed-injection metal organic chemical vapor deposition (PI-MOCVD) was used to deposit thin films of La_2NiO_4 on single crystal YSZ substrates. The nanostructure of the films was investigated by varying the deposition parameters such as substrate temperature[1], frequency and opening time of the injector, the La/Ni ratio in the solvent, and the thickness of the films. The nanostructure was characterized by XRD, SEM and TEM. The La/Ni ratio was varied to study its effect on the activity of the electrode. An excess of La in the film leads to the formation of La_2O_3 which impedes the activity of the electrode. The morphology was tuned from a crystalline, dense thick film to a porous nano-columnar structure by decreasing the substrate temperature (750-600 ˚C) which is in accordance with the Thornton[2] structure zone model. The work is concluded by a discussion of experimental results on the transfer of the optimized deposition conditions from single crystal substrates to freestanding YSZ membranes for µSOFCs.

(1) Stangl, A.; Riaz, A.; Rapenne, L.; Caicedo, J. M.; de Dios Sirvent, J.; Baiutti, F.; Jiménez, C.; Tarancón, A.; Mermoux, M.; Burriel, M. Tailored Nano-Columnar La2NiO4 Cathodes for Improved Electrode Performance. J. Mater. Chem. A ***2022****, 10 (5), 2528–2540. https://doi.org/10.1039/D1TA09110G.*

(2) Thornton, J. A. High Rate Thick Film Growth. Annu. Rev

Exsolved nanoparticles from doped LaAlO3 perovskite: towards lowering the exsolution temperature

Jair G. Triana-Pequeño, Cristian Savaniu & John T. S. Irvine

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In recent years, exsolution has become an alternative to traditional nanocatalyst deposition techniques because it allows for enhanced control over stability, size and distribution e.g. well-anchored and well-distributed metal nanoparticles on the oxide surface without additional processing steps[1]. The exsolution phenomenon can be described as a segregation of metallic nanoparticles from the perovskite oxide B-site lattice to the perovskite oxide surface when the material is exposed to reducing conditions[2,3] or electrical potential. $LaAlO_3$ is a promising perovskite oxide to use as a support for exsolving nanoparticles; despite being less studied than the titanate system, there were some successful attempts to use it for catalytic applications[4,5] and as an anode for Solid Oxide Fuel Cells (SOFC)[6]. The main aim of this work is to significantly reduce the exsolution temperature using doped $LaAlO_3$ as a framework oxide for Solid Oxide Cells (SOCs) electrode applications. Samples with the general formula $LaAl_{1-x}M_xO_{3-\delta}$ (M=Co, Ni or Fe and $0 < x \leq 0.20$) will be synthesised using the modified solid-state route. Afterwards, samples will be reduced in 5% H_2/N_2 at different temperatures. As prepared and reduced samples will be characterised by XRD, TGA, SEM and EDX techniques. Finally, the samples with the highest exsolved nanoparticle densities at the desired processing temperature will be evaluated using ac impedance spectroscopy (IS) and electrochemical testing to determine the material's conductivity and performance for suitable use in a SOC device.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 101017709. http://www.epistore.eu. Twitter: @EpiStoreEU.

References:

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2. Neagu, D., Tsekouras, G., Miller, D. N., Ménard, H. & Irvine, J. T. S. In situ growth of nanoparticles through control of non-stoichiometry. Nat. Chem. 5, 916–917 (2013).

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6. Fu, Q. X., Tietz, F., Lersch, P. & Stöver, D. Evaluation of Sr- and Mn-substituted LaAlO3 as potential SOFC anode materials. Solid State Ionics 177, 1059–1069 (2006).

XPS insight on the improved polymer electrolyte–Li metal interface on high-voltage solid-state batteries driven by additives

Rosalía Cid[1], Ander Orue[1], Mikel Arrese-Igor[1,2], Xavier Júdez[1], Nuria Gómez[1], Juan Miguel López del Amo[1], William Manalastas[3], Madhavi Srinivasan[3,4], Catleya Rojviriya[5], Michel Armand[1], Frédéric Aguesse[1]and Pedro López-Aranguren[1]*

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Solid State Lithium Metal Batteries (SSLMBs) are promising candidates for high-energy-density devices with eliminated safety concerns. They use Li^0 as anode, considered the ultimate replacement for the state-of-the-art graphite anode currently employed in Lithium Ion Batteries (LIBs) for the next generation of rechargeable batteries.[1] However, the lack of stability of Li metal and the propagation of Li dendrites are still outstanding challenges to be addressed for practical applications requiring extended cyclability.[2] Hence, the formation of a robust and stable solid-electrolyte-interphase (SEI) that stabilizes Li metal anode and protects electrolytes is mandatory for the successful development of LMBs.

X-ray photoelectron spectroscopy (XPS) was conducted to characterize the improved SEI driven by LiOH additive on li metal high-voltage cells using $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ active material (NMC622) and poly(ethylene oxide) (PEO) based electrolyte mixed with lithium bis(fluorosulfonyl)imide (LiFSI) salt. XPS analysis showed that the addition of LiOH resulted in an SEI enriched in LiF in the inner part, together with $N\text{-}SO_2\text{-}$ environments (resulting from the labile S-F bond cleavage), while the SEI without LiOH is richer in more reduced sulfur and nitrogen species, probably indicating a higher electrolyte reduction/degradation.[3]

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Building 3D metal anode for Lithium-Ion Batteries

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Environmental pollution and energy crises are boosting the urgent demand for developing next generation rechargeable batteries with high energy density. Lithium (Li) metal anode, with ultrahigh theoretical specific capacity (~3860 mAh g^{-1}), the lowest redox potential (-3.04 V vs. standard hydrogen electrode) and low gravimetric density (0.534 g cm^{-3}), is one of the promising candidates for high-energy-density batteries. However, the growth of Li dendrites during electrochemical cycling, which can cause short-circuit in the cell that potentially results on thermal runaway and explosion, [1] has hindered its application on rechargeable batteries. [2,3] In addition, other challenges associated with Li-metal anodes include volume expansion, poor cycle life, capacity fading, and increased overpotential.

In this study, we propose the use of a 3D copper mesh as substrate for the deposition of Li-metal by thermal evaporation, in order to create a 3D anode to suppress Li-dendrites formation and therefore enabling safe use of Li metal anodes to meet the stringent performance demands of present and future applications. The obtained Li films have been physiochemically characterized to finally carry out the electrochemical analysis of the 3D-system.

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Interfacial Challenges in 3D Thin-Film Li-Ion Batteries by Atomic Layer Deposition

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Atomic layer deposition (ALD) of lithium (Li)-compound thin-films has aroused significant interest in recent years. Promising applications are Li-ion thin-film batteries (TFB), protective particle coatings, interface model systems, and neuromorphic computing [1,2]. Here, we investigate the importance of controlling the interfaces of the battery layer stack fabricated by ALD for three-dimensional (3D) solid-state thin-film batteries to power upcoming autonomous sensor systems.

The simultaneous increase of power and energy density of full cell 3D TFBs by coating the battery layer stack over microstructured substrates was recently demonstrated [3]. The required conformal, pinhole-free deposition and stoichiometric control of nanometer-thin films on highly structured surfaces are only accessible via ALD. The vapor-phase technique based on sequential, self-limiting surface reactions is well understood. However, the direct deposition of Li-compound anodes remains challenging [1].

In previous studies, we developed a thermal three-step ALD process for Li-containing mixed oxides on 200 mm silicon wafers [4, 5]. Lithium-tert-butoxide (LTB) and lithium hexamethyldisilazide (LiHMDS) were both proven as suitable precursors forming high-quality spinel LTO with low impurities after rapid thermal processing.

Here, we examine the influence of interfaces between the current collector, the anode, and solid electrolytes on the electrochemical performance. The surface quality with low contamination of 10 nm titanium nitride (TiN) films by ALD were identified as a critical factor for excellent Li-ion diffusion barrier capabilities [6]. The surface oxidation and texture of TiN strongly influence the subsequent LTO anode. The interface was determined as a key tuning parameter for exceptional C-rate performance up to 200 C of ALD LTO [5]. The outstanding cycle performance, exhibiting only 2 % capacity loss after 1000 cycles at 100 C was linked to excellent uniformity, high-quality interfaces, and superb adhesion of the film. The potential intermixing of LTO with various TiN and solid electrolyte films was investigated in-depth. The superior control of interfaces and stoichiometry of ALD films is a key enabler for high-power 3D TFBs.

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Oxide-ion conductivity and structural disorder of hexagonal perovskites $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ and $Ba_3\mathit{M}NbO_{8.5}$ (*M* = Mo, Nb)

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Hexagonal perovskite-related oxides such as $Ba_7Nb_4MoO_{20}$ and $Ba_3\mathit{M}NbO_{8.5}$ (*M* = Mo, Nb) are attracting much interest due to high oxide-ion conductivity. Bulk conductivity of $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$, 5.8×10^{-4} S cm^{-1}, is remarkably high at 310 °C, [1] and higher than zirconia-based materials. Oxide-ion diffusion in a dense $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ sample was clearly confirmed by the isotope exchange depth profile method, from which we estimated the high oxygen tracer diffusion coefficient D^* value of 7.25×10^{-9} cm^2 s^{-1} at 800 °C (Fig. 1). Rietveld and maximum-entropy method (MEM) analyses of neutron-diffraction data of $Ba_3\mathit{M}NbO_{8.5}$ (*M* = Mo, Nb) up to 800 °C revealed two-dimensional oxide-ion diffusion pathway through the O2 and O3 sites in the intrinsically oxygen deficient layer. Structure analyses also reveal that the O2/O3 disordering makes the minimum NSLD on the O2–O3 path higher (Fig.2), which enhances oxide-ion conductivity.[2]

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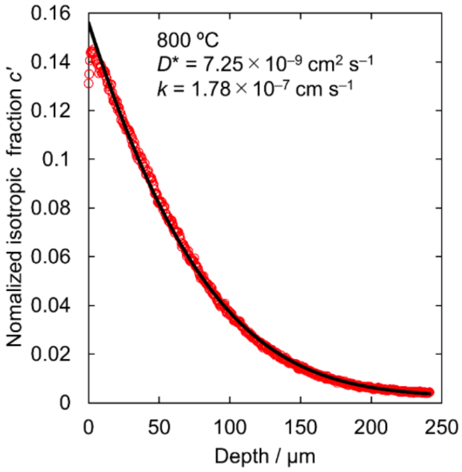

Fig. 1 ^{18}O tracer diffusion profiles for $Ba_7Nb_{3.9}Mo_{1.1}O_{20.05}$ after the exchange at 800 °C for ≃7,200 s with $P(O_2) \simeq$ 200 mbar. Red circles and the black line denote experimental data and the lines of best fit, respectively.

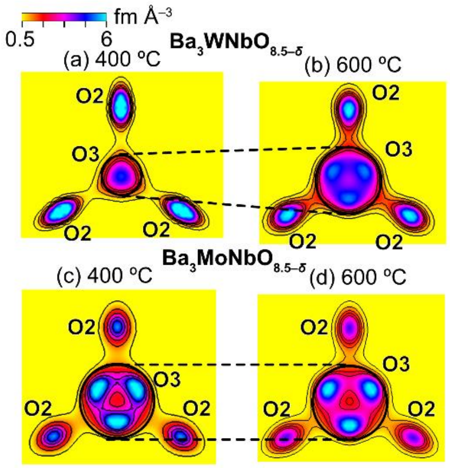

Fig. 2 MEM neutron scattering length density distributions around O2 and O3 sites on the *ab* plane at $z = 0.015$ of (a, b) $Ba_3WNbO_{8.5-\delta}$ and (c, d) $Ba_3MoNbO_{8.5-\delta}$. Contour lines in the ranges of 0.5 – 6 fm Å^{-3} (a,b), from 0.5 to 3 fm Å^{-3} (c,d) (0.5 fm Å^{-3} per step).

Investigating the space charge at mixed ionic and electronic conducting oxide heterojunctions

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Due to the globally increasing energy demand the replacement of fossil fuels by green energy sources is an ever more important challenge. High temperature solid oxide solar cells are one promising regenerative alternative. Together with solid oxide fuel and electrolysis cells they allow generation and storage of electrical energy from sunlight at elevated temperatures. Understanding the underlying processes and reactions of and in such electrochemical systems is a crucial step towards their optimization and development. $SrTiO_3$ (STO) is one promising material for high temperature solid oxide solar cells. Space charge regions at heterojunctions between STO single crystals and various mixed ionic and electronic conductors (MIECs) exhibit high photovoltages of up to 1 V at elevated temperatures. However, models describing the space charge at these MIEC│MIEC interfaces are still less developed than e.g. classical pn-junction models. In this work different mixed conducting thin films ($YBa_2Cu_3O_{7-\delta}$ (YBCO), $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF), $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC), $La_{0.65}Sr_{0.35}MnO_{3-\delta}$ (LSM) and $La_{0.9}Sr_{0.1}CrO_{3-\delta}$ (LSCr)) were grown on (nominally) undoped STO single crystals by pulsed laser deposition. Electrochemical impedance spectroscopy (EIS) was used to investigate the space charge regions at the MIEC│MIEC interface. The extracted space charge potentials are in good agreement with predictions based on defect chemical models (Brouwer diagrams) of the MIEC oxides, i.e., the space charge potential is related to the reducibility of the MIEC. Photovoltages measured upon UV illumination of these MIEC│STO hetero-interfaces are in quantitative agreement with the space charge potentials determined by impedance spectroscopy. Furthermore, X-ray photoelectron spectroscopy also revealed space charge potentials in good agreement with the ones determined by EIS.

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Scalable manufacturing of electrode-supported planar solid oxide electrolizer cells (SOECs)

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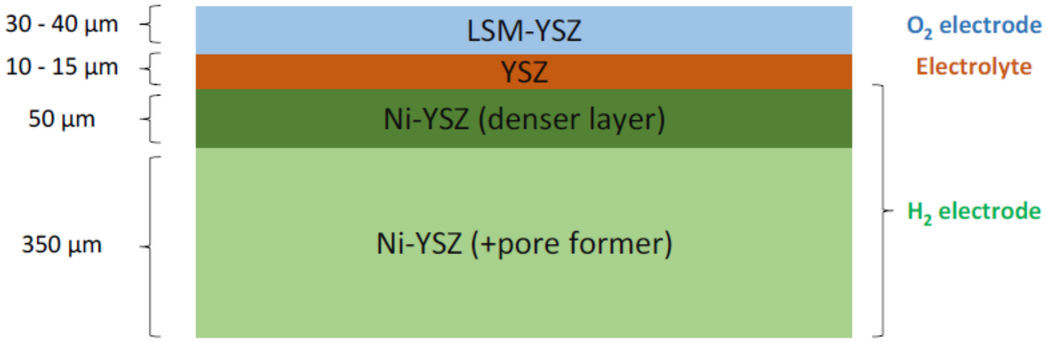
In the near future, electrolyzers will play a central role in converting electrical energy into chemical energy, acting as a link between electric, gas and thermal grid and also providing fuel for transportation. Among the different electrolysis technologies, the Solid Oxide Electrolyzer Cell (SOEC) presents high conversion efficiencies and availability of raw materials [1]. Tubular and planar SOECs are the most common designs, being the planar configuration cheaper and easier to fabricate, and also allows stacking the cells in order to achieve high power densities. However, SOEC commercialization is currently limited by the manufacturing cost [2]. Reducing the operating temperature is critical to improve materials compatibility, reduce energy consumption and start-up time and extend durability. Electrode-supported configurations are the preferred choice, as allow reducing the thickness of the electrolyte and therefore the operation temperature can be diminished [3].

In this work, the manufacturing of planar SOECs of 5x5 cm_2 supported in the H_2-electrode is described. Standard materials were chosen for each component: yttria stabilized zirconia (YSZ) as the electrolyte, Ni-YSZ cermet as the fuel electrode and lanthanum strontium manganite (LSM)-YSZ composite as the oxygen electrode. Screen printing and tape casting were selected as the fabrication methods of the components, taking advantage of its cheapness, scalability and capability of reaching a reduced thickness for the electrolyte (10-15 µm). The figure below is a schematic representation of the fabricated cell, in which the thickness of each component is indicated. The mass transport limitation due to the use of a thick supporting H_2 electrode (~ 350 µm) was offset using a pore former in order to increase the porosity of the electrode. In addition, a denser and thinner layer (~ 50 µm) was employed in contact with the electrolyte.



Schematic representation of the solid oxide electrolysis cell fabricated in this work.

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Investigation and feasibility study of $SrTiO_3$ thin films in high – temperature solid oxide solar cells

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Providing and storing clean energy is getting more and more important fighting global problems like climate change. One way to do so is combining a high temperature solar cell with a solid oxide electrolyzer cell gaining a photoelectrochemical cell, which can be used for small scale energy harvesting applications.

In this study, a high temperature thin film solid oxide solar cell is prepared and investigated to get a better understanding on electrical and defect chemical processes under operation. The preparation is done with pulsed laser deposition (PLD). The solar cell is ablated onto a 10 x 10mm $SrTiO_3$ single crystal in three steps, growing layers of $(La,Sr)CoO_3$ (LSC) (counter electrode), $SrTiO_3$ (STO) (absorber layer) and $(La,Sr)CrO_3$ (LSCr) (working electrode). To analyze the samples, different methods are applied such as electrochemical impedance spectroscopy (EIS), voltage and current measurements under UV light, reciprocal space mapping, transmission electron microscopy (TEM) and mass spectrometry (LA-ICP-MS).

Varying certain parameters like the thickness or the geometry of the STO layer as well as the laser fluence revealed, that the best results can be reached with a STO7% (7% Sr excess in the target [2]) layer with a thickness of about 840 nm using a fluence of ~1 J/cm^2. Voltages up to ~830 mV and currents up to ~0,193 mA/cm^2 were reached under normal atmosphere conditions and 250 °C. Voltages up to ~870 mV and currents up ~0,25 mA/cm^2 are gained under synthetic air conditions at 250 °C.

However, the feasibility of reproducing the samples during preparation poses problems, indicating that the properties of the solar cell are very sensitive to yet unknown preparation parameters.

Acknowledgement: The authors would like to acknowledge the project HarveStore, which is funded by the European Union's Horizon2020 research and innovative programme under grant agreement number 824072.

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High-pressure oxygen in closed pores of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ electrodes

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Morphological changes in the oxygen electrode/electrolyte region as well as delamination of the oxygen electrode may occur during operation of solid oxide electrolysis cells (SOECs) [1-3]. These degradation phenomena are usually explained by the formation of internal oxygen gas: High gas pressures induced by the applied anodic overpotential cause mechanical load in parts of the anode/electrolyte region. However, the current understanding of the nature of this pressure build-up and its relation to the prevailing overpotential and mechanical loads is still incomplete.

In this contribution, we demonstrate that internal oxygen gas pressures can be detected and quantified by analysing the chemical capacitance. For this purpose, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) thin film electrodes with different microstructures were fabricated on yttria-stabilized zirconia (YSZ) single crystals. Very unusual capacitance peaks at overpotentials higher than 100 mV were found following two different pre-treatmeants: i) After annealing electrodes with open inner surfaces (open pores or cracks) for several hours in nominally pure synthetic air, extremely high capacitance peaks in the order of 10 kF/cm^3 were observed. ii) The second pre-treatment involved the application of high anodic bias voltages >750 mV. Electrodes with closed pores, fabricated by depositing a dense LSC capping layer on top of a porous film, showed a capacitance peak already in the pristine state. Closed porosity is a key requirement for the occurrence of this capacitive effect [4]. Based on findings from surface analytical methods and TEM measurements, we explain the correlation of the two described pre-treatments and the occurrence of the capacitance peak by two different degradation mechanisms both causing closed pores. After these degradation phenomena, highly pressurised oxygen forms inside closed pores under anodic polarsiation and leads to the increase of the chemical capacitance. Corresponding model calculations [4] agree very well with the experimental data which reveals gas pressures in the range of 10^4 bar and allows to estimate the amount of closed porosity with high sensitivity (below 0.1 %). Therefore, our method could be used in real SOEC systems for the detection of closed pores and high pressure build-up therein, which may prevent destructive mechanical loads.

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New hexagonal perovskite-related oxides exhibiting high proton conductivity

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Proton conductors attract significant interest, because of their potential uses for protonic ceramic fuel cells (PCFCs), hydrogen separation membranes and gas sensors. $Ba_5Er_2Al_2ZrO_{13}$[1], one of the few proton conductors with hexagonal perovskite-related structure, have oxygen-deficient BaO layers (h′ layers) and show high conductivity without atomic substitution. In this work, we searched for new proton conducting oxides with the h′ layer. Here we report the electrical conductivities and crystal structures of discovered materials. Several Ba_2BMO_5 (*B* and *M* are different cations) materials which have a lower oxygen content than ABO_3 perovskite, were synthesized by solid-state reactions. Total electrical conductivities σ_{total} of the synthesized materials were measured by a DC 4-probe method. We investigated the crystal structure of the new material exhibiting the highest conductivities among the prepared compositions. Crystal structure analysis based on single-crystal X-ray diffraction and neutron diffraction data revealed that the new material is a hexagonal-perovskite related material with h′ layer (Fig. 1). Under the wet condition at 400 ºC, σ_{total} of the new material is almost independent of oxygen partial pressure, and the ion conduction is dominant. The σ_{total} in wet N_2 is higher than σ_{total} in dry N_2. The conductivity ratio of σ_{total} in H_2O saturated air divided by σ_{total} in D_2O saturated air below 800 ºC is close to the expected value for the Grotthus mechanism of proton transport. These results indicate proton conduction of the new material. The bulk proton conductivity of the new material estimated using the AC impedance data is higher than those of $Ba_5Er_2Al_2ZrO_{13}$, novel perovskite $BaZr_{0.8}Y_{0.2}O_{2.9}$ and $BaCe_{0.9}Y_{0.1}O_{2.95}$ (Fig. 2). The proton conductivity is attributable to the dissolution of water in the h′ layers leading to the formation of proton carriers. The result of ab initio molecular dynamics simulations shows that protons mainly diffuse around the c layers between two perovskite layers (Fig. 2).

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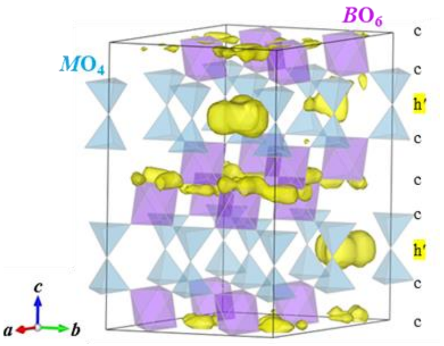

Fig. 1. Refined crystal structure of new material and H+ pobability density distributions (yellow isosurface).

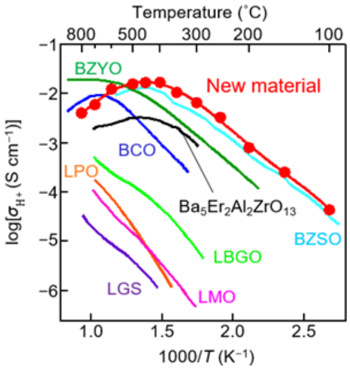

Fig. 2. Comparison of proton conductivity for the new material with those of other proton conductors.

The impact of antisite defects on the oxygen mass transport properties of $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ thin films

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Oxygen mass transport in perovskite oxide thin films is important for many different energy and information technologies. Oxides thin films are often characterized by unintentional cationic nonstoichiometry, which strongly impact their functional properties. Nonetheless, the impact of cation deficiency on the oxygen mass transport properties of oxides thin films is poorly understood. In this work, we investigated the defect compensation mechanism and oxygen transport properties of Mn-deficient $La_{0.8}Sr_{0.2}Mn_yO_{3\pm\delta}$ epitaxial thin films. Oxygen diffusivity and surface exchange coefficients obtained by isotope exchange depth profile technique coupled with secondary ion mass spectrometry (IEDP-SIMS) were observed to be consistent with literature measurements and to be independent on the degree of Mn deficiency in the layers. Defect chemistry modelling, together with a collection of different experimental techniques, suggests that the Mn-deficiency is mainly compensated by the formation of $\mathrm{La}_{\mathrm{Mn}}^{\times}$ antisite defects. The results highlight the importance of antisite defects in perovskite thin films for mitigating cationic nonstoichiometry effects on oxygen mass transport properties.

Additive manufacturing of ceramic nanocomposite fuel cells

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A continual improvement in the synthesis of ceramic nanocomposite materials have revolutionized the ceramic fuel cells with improved performance at a lower temperature (400-600$_\mathrm{o}$C). With the help of an optimized composition of electrolyte material, a record high ionic conductivity of 0.5 S/cm has been achieved at 550$_\mathrm{o}$C. Application of these promising nanomaterials in traditional three-layer fuel cells resulted in ca. 1.1 W/cm$_2$ at 550$_\mathrm{o}$C, whereas application in so called “single-layer cell configuration” resulted in ca. 0.8 W/cm$_2$ at 550$_\mathrm{o}$C. The additive manufacturing including 3D and inkjet printing has the potential to revolutionize the manufacturing of these cells since it can fabricate both the dense and porous structures with good mechanical and electrochemical properties. Inks and pastes of the nanocomposite materials have been developed with appropriate rheological properties and investigated in detail with the dynamic light scattering, viscometer, tensiometry, differential scanning calorimetry and thermal gravimetric analysis. The initial results of our 3D printed nanocomposite electrolytes are very encouraging (0.31 S/cm at 550$_\mathrm{o}$C) and we envision a performance of >2W/cm$_2$ at 550$_\mathrm{o}$C with the help of our robust nanocomposite materials and their fabrication through digital printing. A systematic study is conducted with the help of the state-of-art electrochemical, spectroscopic and microscopic characterization techniques to understand the mechanisms in the cells. Furthermore, effect of sintering temperature was systematically studied to optimize the cell performance. Finally, the stability of these cells is investigated to understand the degradation mechanisms in the cells.

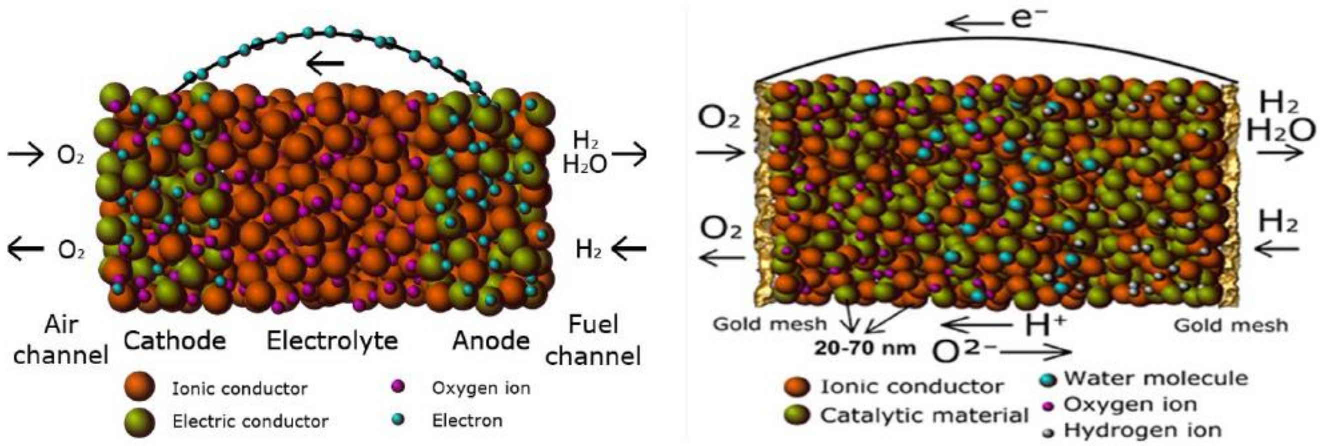

Figure 1: left) Traditional 3-layer ceramic nanocomposite fuel cell, right) Single-layer ceramic fuel cell.

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Visualizing Exsolved Nanoparticles by Anomalous X-ray Scattering Methods

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In recent times, there has been a novel approach for the preparation of advanced metal-supported catalysts which is based on their direct formation by segregation from a perovskite oxide matrix at high temperature and low oxygen partial pressure, known as exsolution (Figure 1). We showed that mesoporous perovskites oxide of the type $La_xSr_{1-x}Ti_{1-y}M_yO_{3-\delta}$ (M = Ni, Co, Fe), synthesized by a modified Pechini synthesis [2], are ideal matrixes for the exsolution process. The large porosity lowers the exsolution kinetics and intrinsically improves the catalytic performance of the catalyst [3]. X-ray powder diffraction and microscopy techniques have proven that the exsolution of these nanoparticles gives rise to catalysts which are socketed onto the substrate, having a narrow size distribution and controlled dispersity. However, for a comprehensive study of the nanoparticle morphology and composition, other techniques should be further adopted.

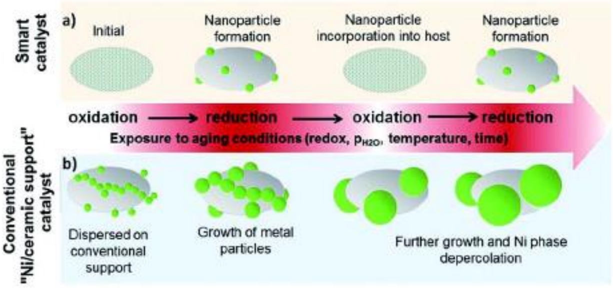

Figure 1: *Comparison of the conventional impregnation and exsolution techniques* [1] .

This study focuses on the use of small angle x-ray scattering (SAXS) and the anomalous SAXS to probe the complex exsolved porous system and obtain overall particle size and particle concentration as well as element selective information such as the composition, and elemental distribution of the nanoparticles in the perovskite matrix. At the atomic scale, ASAXS has proven to be an ideal technique to investigate multimetallic nanostructures by using the so-called resonant or anomalous feature of the atomic scattering amplitude of the target element near its absorption edge to separate its scattering contribution from other elements in the material [4].

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The role of above band-gap radiation on ionic transport at grain-boundaries in Gd-substituted ceria from impedance and tracer diffusion studies

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Until very recently, the use of light radiation has not been considered to impact the concentration or mobilities of defects in crystalline materials. From conventional wisdom, the photon momentum is too low to directly create ionic defects or cause ionic migration, and therefore it is assumed that any changes in observable properties under light radiation should be absent. Several studies, published in recent years, have challenged this assumption. In the hybrid perovskite methylammonium lead iodide (MAPI), above-bandgap radiation enhanced the ionic conductivity by more than two orders of magnitude.[i] This was explained by photo-generated electron-hole pairs modifying the iodine valence state, leading to an increase in anti-Frenkel disorder.[ii] UV radiation has also been reported to induce battery-type voltages in zirconia-based electrochemical cells with $SrTiO_3$ as the working electrode,[iii] and explained by non-stoichiometry changes induced by above-bandgap radiation.[iv] In the latest study on this topic, Defferriere and Klotz et al. demonstrated an enhancement in the specific grain-boundary conductivity of $Gd_{0.03}Ce_{0.97}O_{2-\delta}$ which was attributed to a decrease in blocking space-charge effect at the grain boundaries.[v] The evidence for light-modified behavior of ionic defect is becoming considerable, but a fundamental understanding of these effects is still lacking.

We have carried electrochemical impedance spectroscopy and ^{18}O tracer diffusion on thin films of $Gd_{0.05}Ce_{0.95}O_{2-\delta}$ under a 375nm UV source, corresponding to above bandgap radiation for Gd-substituted ceria. By fabricated films by pulsed laser deposition (PLD) on MgO with a double buffer layer of $BaZrO_3$ and $SrTiO_3$, single crystals of MgO and Al_2O_3, and quartz substrates we can modify the film growth from fully epitaxial, a subset of well-defined grain boundaries, and polycrystalline with a random distribution of grain boundaries. The effect of UV light on the transport of oxygen across grain boundaries of different character can be unambiguously assessed.

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Infrared thermography for thermal transport properties

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Accurate characterization of a thermoelectric material requires measurements of thermo-power, internal electrical- and thermal resistances in the same material and if possible, simultaneously. Such characterization methods are challenging specifically for thin film materials. This paper deals with the use of infrared (IR) thermography as a powerful optical tool to explore the heat fluxes of thermoelectric materials. The infrared (IR) camera constitutes a truly two-dimensional image, allowing for accurate measurements of surface temperature maps in the presence of high spatial gradients. Here, we have used an infrared (IR) thermography to determine the thermal diffusivity of n-type Nb-doped $SrTiO_3$ thin film. We are especially interested in the evolution in time of a temperature field on the thin film micro-device. To determine the thermal diffusivity of the material and thereby the thermal conductivity we have used the experimental results together with a numerical model (COMSOL simulations) to estimate the thermal conductivity of the materials. The overall aim of this work is to illustrate the general principles where IR thermal imaging together with numerical simulation can provide useful experimental results under extreme temperature gradient conditions, which often remain out of reach of conventional thermal properties methods for thin films materials.

Shining light on defect kinetics in mixed-conducting oxide thin films

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Optical approaches for monitoring defect kinetics confer several advantages compared to conventional electrochemical impedance spectroscopy or SIMS tracer profile measurements: they are *contact-free* (enabling study of native surfaces and materials), *continuous* (permitting study of evolution of kinetics over time during structural/chemical transformation), *in-situ*, and relatively low-cost and simple to implement. In many mixed conducting oxides, optical absorption changes at select wavelengths are proportional to defect concentration changes, particularly oxygen and hole concentrations under relatively oxidizing conditions [1]. We leverage this linear relationship (Beer-Lambert law) to monitor defect concentration changes as a function of time by observing the intensity of monochromatic light transmission through thin films continuously up to ~600 °C. In response to a step change of gas atmosphere around the film that sets up a temporary chemical potential gradient, the film stoichiometry re-equilibrates through exchange with the gas, and fitting the corresponding optical relaxation data can quantify surface exchange kinetics for reactions involving redox – assuming the film thickness is well below the critical length. When performed simultaneously with conventional electrical conductivity relaxation, both methods provide equivalent values for the surface exchange coefficients, k_{chem} [2].

In this talk, I would like to provide some examples of our recent applications of this method, including: a) monitoring k_{chem} for oxygen exchange and conductivity changes of perovskite and Ruddlesden-Popper phases based on Fe/Co-substituted $SrTiO_3$ *in-situ* during transformation from amorphous to crystalline structures [3], and b) developing a two-dimensional optical relaxation setup that reveals the spatial extent of enhanced oxygen exchange kinetics at metal-mixed conductor interfaces and permits high-throughput analysis of k_{chem} on combinatorial composition libraries. Results emphasize a) the potential to apply *in-situ*-crystallized mixed conductors in low-to-intermediate temperature energy applications, given their high conductivities and ultrafast oxygen exchange kinetics, and b) the significant impact and risks of using metal current collectors in analysis of MIEC properties. Time permitting, additional capabilities and extensions of defect-light coupling being explored in ongoing work will also be addressed.

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Geometrically Well-Defined Model Systems as a Powerful Tool for a Deeper Understanding of Electrochemical Elementary Processes in Solid Oxide Cell Research

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Solid oxide cells comprise a large class of electrochemical systems with multiple applications in energy conversion (solid oxide fuel and electrolysis cells), heterogeneous catalysis, gas analysis (lambda sensors), electronics (ceramic circuit elements, data memories), and others. The research questions associated with these cells and their materials range from the optimization of commercialized systems to the basic scientific understanding of electrochemical elementary processes. A sound knowledge of the relevant elementary parameters and current pathways is thereby of great importance both for the application case and for purely academic understanding. Identifying these pathways and disentangling elementary parameters such as ionic and electronic conductivities, reaction resistances, interfacial and chemical capacitances is thus the aim of many research works in this field of science.

Well-defined model systems are a powerful tool to achieve this goal, as they offer the opportunity to know exactly the geometry of the model sample and to modify it in a controlled manner. This is the basis for drawing conclusions about current pathways and elementary parameters from electrochemical measurement data and their correlations with geometrical parameters. Moreover, this sample type is an ideal platform for analytical measurements, as the electrochemically active interface is easily accessible by surface sensitive techniques. In the first part of this contribution, two examples are presented, highlighting the abovementioned advantages of model-type thin film samples: *i) Accessibility by surface analytical techniques:* The formation and electrochemical activity switching of exsolution catalysts was studied by a combination of electrochemical techniques and *in-situ* surface analytical measurements. These experiments allowed extensive conclusions to be drawn about both the switching behaviour and the reaction mechanism of H_2 oxidation/H_2O splitting on metal-decorated perovskite electrodes. *ii) Geometrical scalability:* Ni/YSZ pattern electrodes were employed to revisit the question of the triple phase boundary (TPB) activity of this electrode system in H_2/H_2O atmosphere. In addition to confirming the well-accepted TPB path, a second area related reaction resistance could be identified, which now explains so far existing inconsistencies in literature.

In the second part of this talk, it will be shown how the mechanistic understanding obtained on well-defined model-systems can be used to significantly improve the performance of real fuel electrodes in a knowledge-driven manner. By this model-system supported approach it was possible to analytically fit the impedance spectra measured on 3D porous Ni/GDC electrodes by employing a transmission line circuit. This circuit reflects the physically correct relationship of the relevant elementary processes and hence allows separating and quantifying the individual contributions to the electrode polarisation resistance (e.g. ionic conductivity within the porous Ni/GDC network, electrochemical reaction at the GDC surface, among others). With these detailed insights, we can quantitatively explain the excellent performance of our Ni/GDC fuel electrodes, which is enabled by the mixed ion/electron conduction of GDC and their special microstructure. Moreover, it is shown that Ni-free SOFC anode functional layers can even outperform composite anodes, if the functional layer is mixed conducting, sufficiently thin, and good contact to a current collecting layer is established.

Micro and Nanotechnologies for autonomous devices

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Information society is responsible for the progress of our civilization. It is based on computing and their integrated circuits whose development has benefited from the miniaturization, the reproducibility and the scalability of Si based micro and nanotechnologies (MNTs). This progress has come, however, with an increasing and unsustainable demand of energy that requires new paradigms. The future solutions for energy generation will, ideally, be based on abundant and non-toxic materials, on efficient harvesting, and their compatibility with powering portable devices. The possibility to combine the advances in materials developments with Si based MNTs based integration opens new routes to exploring innovative device architectures and technologies to solve these challenges.

Micro-Electro-Mechanical Systems (MEMS) can be defined as the set of miniaturized devices and structures that combine electrical and mechanical elements developed using the techniques of microfabrication. MEMS technologies complement standard thin film Si technologies and allow the definition onto Si substrates of free volume of surfaces that enable a non-electronic interaction (e.g. mechanical, thermal, chemical, optical) with the surrounding environment. MEMS production lines are more amenable to heterogeneous integration of materials than pure IC ones.

Here we overview our group's effort to enable some of these devices. First, we will discuss device technologies for the integration of micro solid oxide fuel cells (μSOFCs) with MEMS technologies and present a micro reforming unit for the conversion of fuel. The μSOFCs are becoming a strong candidate beyond Li-technologies because of their high energy density, efficiency and open the possibility to the use of different fuels, such as hydrocarbons [1-3]. However, their integration on autonomous devices depends on the correct route of miniaturization. One of the most promising approaches is focused on the monolithic integration of functional components (e.g. electrolytes, electrodes, current collectors) in Si technology. Even for components not made of silicon, this approach ensures a high reproducibility and reliability, a cost-effective mass production and an easy integration in the semiconductor industry.

Second, we will discuss a micro thermoelectric generator (μTEG) based on Si nanowires that is able to generate power outputs in the range of 10-100 µW/cm2, which may meet of the requirements of a node in the Internet of Things (IoT). Si nanomaterials show a good thermoelectric performance themselves. It is the case of Si nanowires or nanostructured thin films that, due to their reduced dimensions, present an increment on phonon scattering and, in consequence, a reduction on thermal conductivity of several orders of magnitude. These Si nanomaterials can be integrated with micro and nano technologies for the fabrication of high performance Si-based μTEGs [4].

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Photocatalytic water splitting with oxynitride semiconductors: in situ and operando characterizations of the solid-liquid interface

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H2, as a sustainable and carbon-free energy carrier, can be produced using sunlight to photogenerate electron/hole pairs capable of driving the electrochemical reactions of water reduction and oxidation. This photoelectrochemical process of water splitting is commonly known as artificial photosynthesis.

Several oxynitride semiconductors meet many of the stringent material requirements needed to produce H2 using sunlight. However, there are still many open challenges to be addressed before this photoelectrochemical mechanism can become ripe for practical technological applications.

Charge generation and migration in the semiconductor is an important aspect. Furthermore, when the charge carriers reach the surface of the semiconductor, in contact with water, they must be readily available to trigger the water splitting electrochemical processes. The solid-liquid interface is where electrochemistry takes place, but it is at the same time a very difficult local environment to probe under operating conditions.

With this contribution, I would like to share with you our research efforts towards the development of experimental tools and strategies that allow us to obtain information on the physicochemical evolution of the solid-liquid interface. In particular, I will discuss the characterization opportunities offered by *operando* and *in situ* surface-sensitive X-ray absorption spectroscopy and neutron reflectometry.

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High-Throughput Investigation of Combinatorial Thin Film Ternary System as Electrolytes for Protonic Ceramic Cells

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The research of efficient and innovative materials for protonic ceramic cells requires the characterization of countless compositions. A high-throughput approach was chosen to initially evaluate the electrochemical performance of hundreds of compositions inside the ternary plot $Ba(Ce,Sn,Zr)_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCSZYY).

The thin film combinatorial library was produced by pulsed laser deposition on top of Si(100) single crystal substrate with a 100 mm diameter (Fig. 1A). The composition gradient is obtained through alternate depositions of $BaCe_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCYY), $BaSn_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BSYY) and $BaZr_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZYY) centered on the edges of the substrate. The thickness of thin film deposition was characterized by XY-resolved spectroscopic ellipsometry in a photon energy range of 1.5-4.5 eV. The deposition centers for each target material correspond to the maximum values, i.e., 220 nm for BCYY and BSYY and 200 nm for BZYY (Fig. 1B). XY-resolved X-ray diffraction was performed to study the deposition structure. A Matlab code was developed to analyze all the XRD patterns and calculate the cell parameters of the thin film using a pseudocubic structure. The resulting values of the *a* cell parameters range from 4.1759 Å for the BSYY-rich part, to 4.2508 Å for the BZYY area, up to 4.4189 Å for the BCYY one (Fig. 1C), in good accordance with the values obtained by Rietveld refinement for reference powders of single materials.

A custom-made furnace was developed and calibrated for the compositional and structural analysis in dry and wet conditions at high temperature. A custom-made setup for electrochemical impedance spectroscopy is under development to measure the electrochemical performances as proton conductor electrolyte.

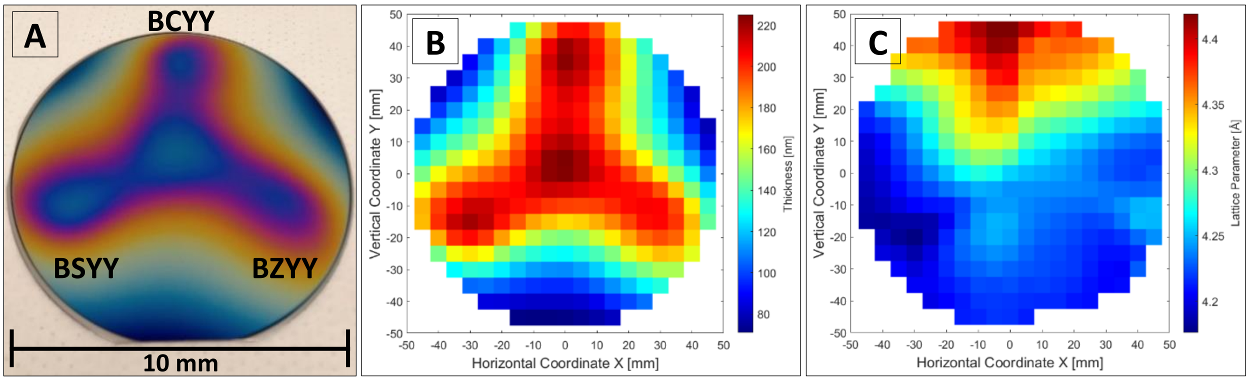

Figure 1. A: Photo of the BCSYY thin film library. **B**: Map of the deposition thickness measured with Spectroscopic Ellipsometry. **C**: Map of the pseudocubic *a* cell parameter of BCSZYY.

Defect Chemistry of Lanthanum Ferrite Thin Films during Ion Intercalation in alkaline electrolytes

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Ion intercalation of perovskite oxides in liquid electrolytes is a promising method for controlling their functional properties while storing charge, with potential application in different energy and information technologies. Although the role of defect chemistry in the ionic incorporation in a gaseous environment is well established, its impact in the ion intercalation in liquid electrolytes at room temperature is poorly understood. In this talk, we will present the study of the evolution of point defects of $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ thin films subjected to an electrochemical bias in alkaline electrolytes. Through a collection of different experimental techniques, we found that both oxygen and protons are intercalating in the layers at moderate electrochemical potentials, giving rise to a change in the oxidation state of Fe as a charge compensation mechanism. The variation of the holes concentration as a function of intercalation potential was characterized by in-situ ellipsometry and the concentration of electron holes were indirectly quantified for different electrochemical potential. Finally, we show that the evolution of electronic holes is well described by a diluted defect chemistry model, involving oxygenation and hydration reactions. The results provide new insights into the role of defect chemistry during ionic intercalation of perovskite oxides in alkaline media.

High-throughput methodologies for the study of cathodes in solid oxide cells: the $La_{0.8}Sr_{0.2}Co_xMn_yFe_{1-x-y}O_3$ perovskite family

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As research on materials science and in particular on solid oxide cells progresses, the need for more advanced, systematic and effective methodologies for discovering novel materials and their application areas becomes evident. The development of high-throughput tools for screening complete formulation families has risen as a compelling approach for satisfying this need. These tools make it possible to synthesize and characterize a whole set of samples in a single run, ensuring the same experimental conditions in every measurement and enabling more efficient materials screening.

Here, we report on a systematic study of the $La_{0.8}Sr_{0.2}Co_xMn_yFe_{1-x-y}O_3$ (LSCMF) perovskite ternary system of air electrodes. Combinatorial pulsed laser deposition was employed on the parent materials (i.e. LSC, LSM and LSF), resulting in the growth of a thin film wafer with graded composition. The three single-phase target materials were alternatively deposited on opposite edges of the substrate at high temperature. The formation of an intermixed layer that contains the compositions of the whole ternary diagram was obtained in a single deposition run. The multicomponent sample was characterized by X-ray diffraction, X-ray fluorescence spectroscopy, Raman spectroscopy and spectroscopic ellipsometry, allowing mapping of the structural, crystallographic and electronic properties (e.g. lattice parameter, Raman shift peak and optical absorption coefficient). Most interestingly, the electrochemical performance of the whole system was measured at once by impedance spectroscopy using an automated large-area high temperature testing station. This setup allowed the simultaneous recording of the area specific resistance of the thin film at a given temperature and for each composition. The results obtained pave the way to a deeper understanding of the LSMCF cathode family based on the correlation of structural and electrochemical properties for a wide materials space, as well as setting up a general methodology for high-throughput research of electrochemical materials.

Rechargeable oxide ion batteries based on mixed conducting intercalation electrodes

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Mixed conducting oxides are frequently studied as electrode materials for solid oxide fuel or electrolysis cells. However, their ability to change stoichiometry depending on the oxygen chemical potential also enables charge storage typical for battery electrodes: Formally neutral oxygen can be incorporated by annihilating oxygen vacancies and creating electron holes, similar to the intercalation of lithium in lithium ion battery electrodes. Electrodes with different reducibility of the oxide should thus allow operation of an oxide ion battery. This is exemplified for perovskite-type $La0.6Sr0.4FeO3-\delta$ (LSF), $La0.5Sr0.5Cr0.2Mn0.8O3-\delta$ (LSCrMn)and $La0.9Sr0.1CrO3-\delta$ (LSCr) electrodes with blocked oxygen exchange at the surface. Cells with thin film electrodes were grown by pulsed laser deposition on yttria stabilized zirconia single crystal electrolytes. Charge/discharge cycles and impedance measurements were performed on half cells between 350 and 500 °C and related to the materials defect chemistry. Electrode capacities of up to 350 mAh/cm^3 and less than 0.25 % capacity loss over 19 cycles were measured at potentials between 0.2 and -1.1 V vs. O2 at 1 bar. Full cells with LSF cathodes and LSCrMn anodes were successfully operated at 350 to 400 °C with electrode related energy densities up to 70 mWh/cm^3, coulomb efficiencies >99 % and good cycling performance. This novel type of rechargeable battery may open further application fields such as elevated temperatures (>200 °C), where common cation-based intercalation cells are not applicable so far.

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Direct electrocatalytic CO2 reduction in a tubular protonic membrane reactor

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Integration of membranes into reactors create the opportunity to increase the yield for CO_2 reactions as well as the potential to increase energy efficiency for the production of carbon neutral synthetic liquid fuels. In this work, developed in the frame of the eCOCO2 project, towards further process intensification via the direct electrochemical synthesis of long chain hydrocarbons, also the CO_2 reduction into methane was studied in a tubular protonic membrane reactor composed of (i) $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_3$ as electrolyte and (ii) $Ni+BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$ as electrodes, that allows the proton injection in the reaction chamber. Hydrogen pumping, CO_2 conversion, CH_4 yield, impedance spectroscopy and voltage distributions were studied as a function of the applied current density and the operational conditions (at 450 ºC and pressures ranging from 1 to 30 bar). Total pressure plays an important role in both CO_2 conversion and CH_4 selectivity that deeply increase when pressure is risen (Figure 1a). Additionally, computational fluid-dynamics (CFD) simulations were employed to optimize the reactor performance and to validate the experimental data with the modelling. These results provide critical knowledge about the thermodynamics, transport phenomena and electrochemical performance of membrane reactors for electrocatalytic CO_2 reduction.

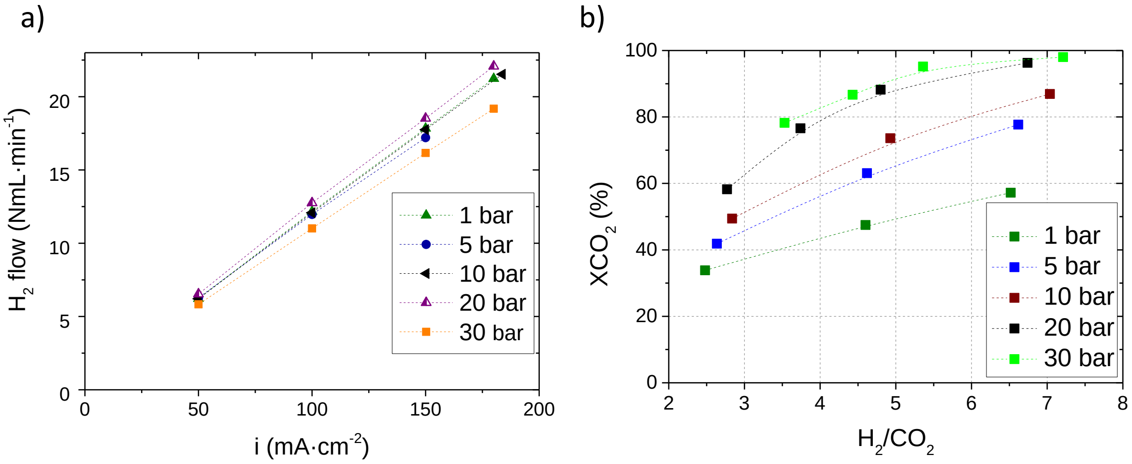

Figure 1. H_2 flow as a function of the pressure and applied current density (a) and CO_2 conversion into methane as a function of the pressure (b) obtained using a tubular protonic membrane reactor.

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A Cobalt-based nanocomposite for increased electrochemical stability at high temperature in Solid Oxide Fuel Cell

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Thin Film Solid Oxide Fuel Cells (TF-SOFC) have received attention as a potentially useful technology for ultracompact energy conversion and storage. For these devices, high ionic conductivity and electrochemical activity of the electrodes are required. More specifically, it has been extensively documented that oxygen reduction reaction (ORR) at the air electrode side acts as a barrier for the device overall performance. Mixed Ionic and Electronic Conductors (MIECs) were found to enhance the overall performances of SOFC devices when applied as air electrodes. Nanoengineering of MIECs can help opening the door to a wide range of nanostructures by controlling the electrochemical activity and reducing the negative effects that cathode materials experience at the typical operation temperatures they undergo in SOFCs (around 700-900ºC).

The fabrication of a nanocomposite of lanthanum strontium cobaltite (LSC, $La_{1-x}Sr_xCoO_3$ with x = 0.2, 0.4) and doped ceria (SDC, 20% Sm) was used in this study to improve the electrochemical performances at high temperature over time when compared to the single-phase perovskite-based air electrode (LSC). Pulsed Laser Deposition (PLD) was used to produce thin film nanocomposites from a homemade target using mixed powders of the two materials. For the nanocomposite electrode and a reference cobaltite cathode, microstructural characterizations by High Resolution X-Ray Diffraction (HR-XRD), imaging by scanning electron microscope (SEM) and transmission electron microscope (TEM), and surface analysis by X-Ray Photoelectron Spectroscopy (XPS) of the films were collected. For both materials, an Electrochemical Impedance Spectroscopy (EIS) analysis was performed during ageing until 100 hours at 700ºC. Main results emerging from the electrochemical study demonstrated an enhancement in the polarization resistance (Rp) stability over time with the nanocomposite (LSC-SDC) experiencing a lowering in Rp of about 20% of the initial value in the first 5 hours and maintaining the value significantly constant during the overall measurement, while the reference material (LSC) exhibit an initial lower Rp value which rapidly increase to over 100% of its initial value due to degradation caused by Sr segregation. Further steps of this work involve transferring the nanocomposite fabrication to large area Ni/YSZ-based cells in order to test the electrochemical output given by the nanocomposite in real SOFC conditions.

Bismuth niobium oxychloride, Bi4NbO8Cl, as a New Layered Oxide Ion Conductor

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Oxide-ion conductor is an important functional material and widely used in various electrochemical devices such as solid oxide fuel cells, high temperature electrolyzer, gas sensors, and oxygen separating membranes. It is reported that Bi_2O_3 doped with Y_2O_3 shows the highest oxide ion conductivity in high P_{O2} range among the doped Bi_2O_3 family ($\log\sigma$(S/cm) = 0.47 at 1073K in air). On the other hand, c-$Bi_4V_2O_{11}$ (parent of the so-called BIMEVOX materials), which belongs to the Aurivillius series also shows the higher oxide ion conductivity Sillén-Aurivillius type oxychlorides, which are layered compounds containing perovskite layers sandwiched between bismuth oxide layers and halide layers as shown in Fig.1, and were initially explored for their photocatalytic properties [1] despite the closely related Aurivillius type oxides like the metal-doped bismuth vanadium system BIMEVOX.

Oxide ion conductivity in Sillén-Aurivillius phase, bismuth niobium oxychloride (Bi_4NbO_8Cl) was studied. Although it is well-known that Bi base oxide shows high oxide ion conductivity within narrow P_{O2} range, it was found that Bi_4NbO_8Cl shows high and rather stable oxide ion conductivity over wide PO2 range (down to 10-19 atm) and doping Sr to Bi site in Bi4NbO8Cl is effective for increasing oxide ion conductivity among the examined dopants. The optimized oxide ion conductivity was achieved at x=0.1 in Bi4-xSrxNbO8Cl. The ionic transport number of this oxide is close to unity from AC impedance measurement, EMF on gas concentration cell and the tracer oxygen diffusion measurement. Considering the activation energy of self-diffusion constant and grain conductivity, oxide ion may be mainly diffused along Bi2O22+ layer and the choline layer may interrupt the diffusion of oxide ion because of electrostatic repulsion. Therefore, oxide ion conductivity in Bi4-xSrxNbO8Cl could be two dimensional, however, Cl layer in Sillén-Aurivillius phase may contribute the increased stability in reducing atmosphere. Consequently, this study reveals that Bi4NbO4Cl is a new family of oxide ion conductor and conductivity is comparable with LSGM.

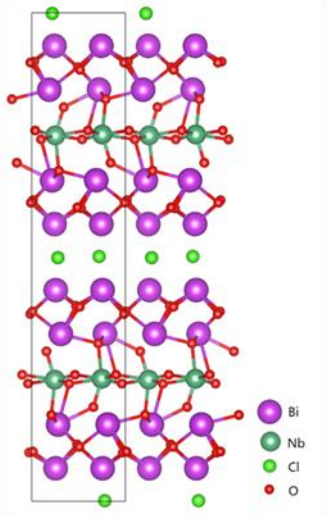

Fig. 1 Crystal structure of Bi_4NbO_8Cl

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New Oxide-ion Conductors of the Dion–Jacobson phases CsM2Ti2NbO10−δ (M = Bi, La)

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Oxide-ion conductors have received considerable attention owing to their wide applicability in many electrochemical devices such as solid-oxide fuel cells, oxygen gas sensors, and oxygen separation membranes. Dion–Jacobson phases are known for their rich magnetic and electrical properties; however, there have been no reports on oxide-ion conduction in this family of materials. Here, for the first time to the best of our knowledge, we show the observation of fast oxygen anionic conducting behavior in $CsM_2Ti_2NbO_{10-\delta}$ (M = Bi and La).[1,2] Interestingly, the bulk ionic conductivity of this Dion–Jacobson phase $CsBi_2Ti_2NbO_{10-\delta}$ is 8.9×10^{-2} S cm^{-1} at 1073 K, a level that is higher than that of the conventional yttria-stabilized zirconia (YSZ) (**Fig. 1**). The high oxide-ion conductivities of $CsBi_2Ti_2NbO_{10-\delta}$ are attributable to (i) the large anisotropic thermal motions of the oxygen atoms in the inner oxide-ion conducting perovskite layer, (ii) the two-dimensional O1–O2 and O1–O1 oxide-ion diffusion, (iii) the presence of oxygen vacancies and (iv) the large bottlenecks. We have also proposed a concept: large bottlenecks for oxide-ion migration by large size of Cs^+ and Bi^{3+} displacement (**Fig. 2**). Indeed, the oxide-ion conductivity has been improved by substitution of Sr for Bi in Dion-Jacobson phase $CsBi_2Ti_2NbO_{10-\delta}$. [3] The present finding of high oxide-ion conductivity in Dion–Jacobson phases suggests the potential of Dion–Jacobson phases as a platform to identify superior oxide-ion conductors.

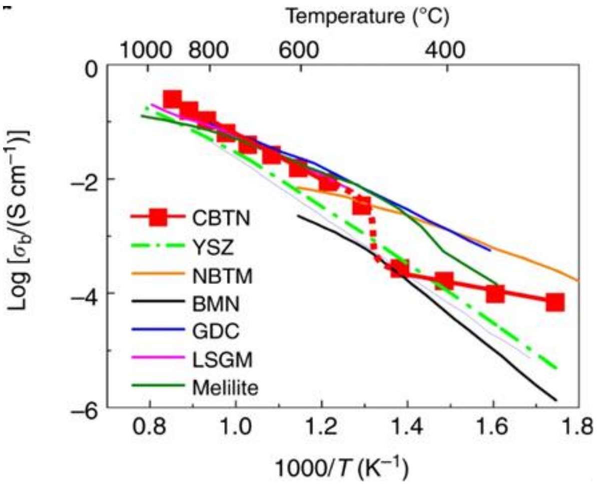

Fig. 1 Comparison of bulk conductivity σ_b of $CsBi_2Ti_2NbO_{10-\delta}$ (CBTN) with those of best oxide-ion conductors.

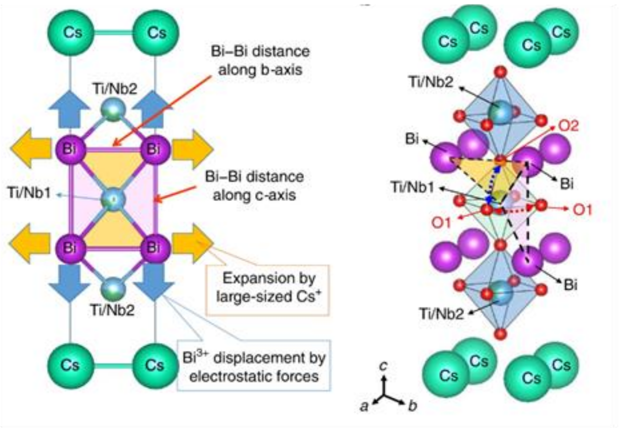

Fig. 2 New concept of enlarged bottlenecks for oxide-ion migration created by large size of Cs^+ and Bi^{3+} displacement in $CsBi_2Ti_2NbO_{10-\delta}$.

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The effect of operating environments on surface composition evolution of perovskite-type mixed conducting electrodes

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The ability of mixed ionic and electronic conducting (MIEC) perovskite oxides (ABO3) to support both electronic and ionic conductivity, as well as their favourable catalytic properties and chemical and redox stability, make them promising electrode materials in electrochemical energy conversion devices, such as solid oxide fuel/electrolysis cells (SOFC/SOEC) and oxygen transport membranes (OTM). In these applications, the exchange of oxygen across the gas phase and an electrode often determines the overall device performance, and the surface exchange kinetics have been found strongly related to the surface composition of electrodes. Currently, the nature of these electrode surfaces, particularly under the gas atmospheres closer to those experienced in operation, still remains unexplored. In this work, taking (La0.8Sr0.2)0.95Cr0.5Fe0.5O3-δ (LSCrF8255) as a model MIEC perovskite oxide, the surface composition evolution was studied under dry oxygen (pO2 = 200 mbar), wet oxygen (pO2 = 200 mbar, pH2O = 30 mbar), and water vapour (pO2 < 1 mbar, pH2O = 30 mbar) environments, to reflect the implementation of the materials for oxygen reduction/evolution and H2O electrolysis in the applications mentioned above.

The surface chemistry and morphology of the materials were investigated comprehensively through X-ray photoelectron spectroscopy (XPS), angle-resolved XPS (ARXPS), low energy ion scattering (LEIS), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM). The Sr surface segregation phenomenon has been observed on surface of all the samples annealed in dry oxygen, wet oxygen, and water vapour. The segregation level increased with annealing temperature, and was found particularly high at 900 °C. For the samples annealed at 900 °C in different atmospheres with the same 27-hour annealing time, the surface of the sample annealed in water vapour displayed the highest atomic fraction of Sr in surface species compared to Sr in the perovskite structure, however, the surface of the sample annealed in dry oxygen showed the highest total Sr content. Meanwhile, on the sample annealed in wet oxygen, Sr surface enrichment was likely suppressed. In addition, the Sr segregation phenomenon observed on LSCrF8255 can be correlated to other mass transport phenomena such as Cr evaporation and redeposition and Si deposition. Further, the Sr segregation behaviour on LSCrF8255 can also be related to annealing duration, crystal orientation, and defects such as grain boundaries and dislocations. Apart from the A-site cation segregation, a phase separation was consistently observed on all samples annealed in the three conditions. The secondary phase was B-site cation (relatively Cr enriched, significantly Fe enriched) enriched and A-site cation (La and Sr) deficient. In addition, in contrast to the Sr enriched surface, a La enriched surface was observed on samples annealed in dry oxygen at 600 and 700 °C, which was found to be potentially caused by the Sr and Cr surface evaporation processes. Our scientific findings are expected to provide an advancement in understanding and guidelines for material design, performance, and durability of MIEC perovskite oxide applications.

Bimetallic exsolution from perovskite oxides: an insight on mechanistic aspects through in-situ measurements for tailoring catalytic selectivity

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Bimetallic exsolution in perovskite oxides has recently developed increasing interest in heterogeneous catalysis for environmental and sustainable energy applications. This is related to the possibility of regenerating these materials through simple re-oxidation, and to the flexibility in tailoring their catalytic properties given by the synergistic effects that lie behind the exsolution process of two or more metals. In this work, in-situ XANES and synchrotron XRD have been used for the analysis on Ni-Fe doped, 20% A-site deficient strontium titanates (La0.4Sr0.4Ti0.60Fe0.35Ni0.05O3), in order to investigate the processes of reduction and nucleation of metal nanoparticles throughout the exsolution process and the effect of the temperature on the kinetics of exsolution. This allowed to point out how the stages of reduction of the exsolved B-site metal species (namely Fe0 and Ni0) and the nucleation/growth of the metal nanoparticles on the materials surface constitute two separate, yet interconnected processes. Moreover, the structural and catalytic properties of these materials can be modified by varying the exsolution conditions, such as temperature, time of treatment and oxygen partial pressure. This feature assumes major interest in many catalytic applications, in the light of the chance of adjsuting the nanoparticles composition and regenerating them through redox cycling. In particular, the catalytic performances of the supported Ni-Fe nanoparticles with respect to dry ethane reforming (DER) and ethane oxidative dehydrogenation (ODH) have been studied in this work. The outcome of the catalytic tests demonstrated the switchable nature of such materials, and pointed out the possibility of acting on the exsolution operative parameters for tailoring the catalysts selectivity towards the desired products. Moreover, this system showed stable catalytic performances over 10 hours of time-on-stream operation, with improved resistance to deactivation and enhanced selectivity towards a valuable product such as ethylene, when compared to commercially available supported metal catalysts.

Tuning ternary alloyed nanoparticle composition by exsolution

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Due to the important correlation between global warming and increasing atmospheric concentrations of greenhouse gases (GHGs), like CO_2, it is imperative to develop a more sustainable energy supply system. In this context, solid oxide electrolytic cells (SOECs) are becoming a promising alternative as energy conversion devices. State-of-the-art fuel electrode Ni-YSZ suffers from coking and sintering in long-term operation. Thus, SOEC electrode composition is being widely studied to solve these problems. Mixed ionic-electronic conducting (MIEC) perovskite materials proved higher electrocatalytic activity for CO_2 reduction, especially iron-containing materials, such as $Sr_2Fe_{1.5}Mo_{0.5}O_6$. To functionalize these alternative fuel electrodes, exsolution emerges as a promising alternative to classical impregnation methods. Exsolution allows the formation of metal nanoparticles (NPs) by applying reducing conditions at high temperatures, which remain anchored to the surface of the original oxide support improving their stability, distribution, and preventing high-temperature sintering issues. Isomorphic substitution of B-site cations, combined with exsolution, appears to be an interesting strategy to improve the performance of this kind of electrodes due to the possibility of exsolving alloyed metallic nanoparticles.

In this work medium-entropy double perovskite system $Sr_xFeCo_{0.2}Ni_{0.2}Mn_{0.1}Mo_{0.5}O_{6-\delta}$ (x = 2.0, 1.9, 1.8) was studied to prepare cathodes for SOECs with enhanced electrocatalytic activity. B-site Fe substitution with Co and Ni lead to Fe-Co-Ni ternary alloyed nanoparticles (Fig.1) with different compositions and sizes depending on the exsolution temperature. Therefore, we prove for the first time the alloyed exsolved nanoparticle composition can be tuned by adjusting the reducing conditions. Then, we studied the electrocatalytic activity of $Sr_2FeCo_{0.2}Ni_{0.2}Mn_{0.1}Mo_{0.5}O_6$ for direct CO_2 electrolysis, revealing the catalytic enhancing effects of exsolved Ni-Fe-Co nanoparticles with high Faradaic effieciencies. In summary, here we proved the possibility of obtaining ternary alloy nanoparticles that boost the electrocatalytic activity of SOEC electrodes. Our results show that nanoparticle size and composition can be easily adjusted by controlling the exsolution parameters.

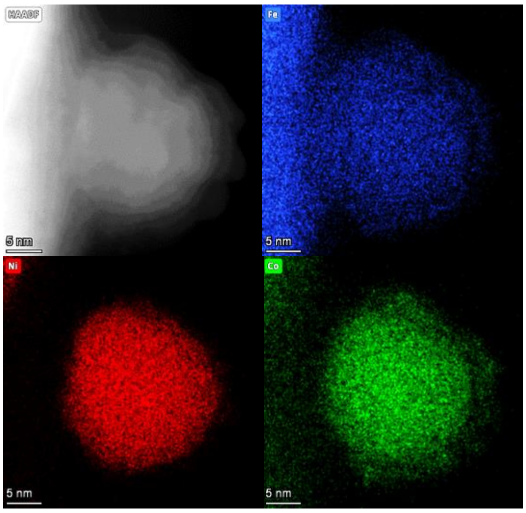

Figure 1.HAADF-STEM and XEDS maps of x=2.0 composition exsolved nanoparticle (800ºC)

Towards High-Performance, Low-Temperature Solid Oxide Cells with Vertically Aligned Nanocomposite Films

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Low temperature solid oxide cells (SOCs) represent a key technology in next-generation energy devices for portable applications, offering the highly efficient conversion of electrical to chemical energy, and vice versa. To date however, the widespread implementation of SOCs has been prohibited by excessive polarisation resistances at the device electrodes, despite significant progress in materials design.

Vertically aligned nanocomposite (VAN) films have been a leading class of materials in recent performance enhancements in SOC design, and in this work we further explore the growth and characterisation of such VAN films. State-of-the-art fluorite and perovskite materials are combined in each of the anode, electrolyte, and cathode layers and the enhancement rendered by the novel VAN structure quantified in each case by electrochemical impedance spectroscopy (EIS). Moreover, films are grown on both single-crystal and more commercially viable polycrystalline/amorphous substrates. This allows for a detailed study of the VAN growth mechanisms for materials of differing crystal structures, while also giving an improved understanding of the importance of crystalline perfection in thin-film SOC device performance.

Future progress in low-temperature SOC technology will rely heavily on a detailed understanding of the growth mechanisms of state-of-the-art nanostructured materials, such as VAN thin films. By building such an understanding and quantifying the performance enhancements resulting from a wide variety of VAN structures, this study represents an important step towards the realisation of efficient low-temperature SOCs for portable applications.

Modeling Defects in Polycrystalline Materials

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The functionality of the materials used for energy applications is critically determined by the physical properties of small active regions such as dopants, dislocations, interfaces, grain boundaries, etc. The capability to manipulate and utilize the inevitable disorder in materials, whether due to the finite-dimensional defects (such as vacancies, dopants, grain boundaries) or due to the complete atomic randomness (as in amorphous materials), can bring innovation in designing energy materials. With the increase in computational material science capabilities, it is now possible to understand the complexity present in materials due to various defects resulting in pathways required for optimizing their efficiencies. In this talk, I will provide a critical overview of such computational advancements specifically for designing realistic materials with various types of defects. I will discuss the traditional approaches (implemented via tools such as density functional theory, and molecular dynamics) as well as modern approaches such as machine learning that exist for understanding the impact of defects in polycrystalline materials, thereby identifying future opportunities for energy materials design and discovery.

Acknowledgments

The author acknowledges the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery grant program, Canada Research Chair (CRC) program, the Canada Foundation for Innovation (CFI) for infrastructure and operating funds. Computations were performed on the HPC supercomputer at the Calcul Québec (https://www.calculquebec.ca) and Compute Canada (www.computecanada.ca).

Recipes for superior ionic conductivities in thin-film ceria-based electrolytes

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Improving the overall performance of a solid oxide fuel cell (SOFC) involves, in many cases, increases in the rates of oxide-ion transport displayed by the electrolyte and electrode materials. This aim becomes particularly critical in the case of the Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC): improved performance at ever lower operating temperatures is required, but lower temperatures mean lower rates of (thermally activated) oxide-ion transport. This can be offset partly by reducing its thickness, since its resistance is the important factor. New possibilities to offset the lower operating temperatures would, therefore, be extremely welcome.

In this study [1], we utilised a powerful combination of two well-established simulation methods — molecular dynamics (MD) and Metropolis Monte Carlo (MMC) — and applied them to one of the best electrolyte materials for IT-SOFC — $Ce_{1-y}Gd_yO_{2-y/2}$. The MMC simulations were used to generate equilibrium distributions of the substituted Gd cations that were compared with random distributions of Gd. The former are similar to those found in sintered ceramics (a point often neglected in many computational studies). MD simulations allowed us to extract the ion mobilities as a function of electric field and temperature directly, a task that is non-trivial for highly concentrated solid solutions.

Two important findings emerged from our results: In all cases studied, the random distribution displayed a higher conductivity than the equilibrium distribution, with the difference being up to an order of magnitude. Second, the reduction of the film thickness to a few nanometres and the use of an operating voltage of only 1 V can lead to an additional increase in the conductivity by an order of magnitude due to nonlinear field effects. Additionally, we established an analytical model that describes all the conductivity data. On this basis, we can predict the conductivity at different concentrations, field strengths and temperatures.

Thus, with our study, we provide two new recipes for the development of superior ceria-based thin-film electrolytes for use in IT-SOFC. We showed that field-enhanced ion transport is possible in these electrolytes at physically realistic voltages and film thicknesses, and, in combination with maintaining a random Gd substituent distribution, can lead to tremendous increases in ionic conductivity.

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Molecular Dynamics Study of Oxygen-Ion Diffusion in Yttria-Stabilized Zirconia Grain Boundaries

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SOFC technology currently suffers from material interaction, insulating phase formation, and thermal stresses as it operates at high temperatures, which results in rapid degradation, low reliability, and high cost for commercialization. One of the approaches to reduce the operating temperature of SOFCs is the use of thin-film electrolytes to reduce the ohmic losses experienced at a reduced temperature while offering high thermal stability. That been said, the nanoscale thin films are generally polycrystalline and contain a high density of Grain Boundaries (GBs), which can substantially affect the ion diffusion in electrolytes. Experimentally, the atomistic structure of GBs can be analyzed and observed via high-resolution scanning TEM, but unfortunately, it does not provide sufficient information about the atomic-level structure of these boundaries. Molecular Dynamics (MD) simulations have been used for studying Grain Boundaries' atomic structure and oxygen-ions transport across YSZ electrolyte over the last decades. However, high symmetry GBs have been commonly targeted even though most boundaries found in polycrystalline samples are a mix of twisted and tilted denominations- commonly named "mixed" GBs. A mixed grain boundary (GB) was modelled at the atomic level using MD in this work. The structure was built from a TEM image of an 8YSZ thin film sample using the amorphization and recrystallization (A&R) technique. Oxygen-ion self-diffusion was studied for a range of temperatures between 700 K and 2300 K and Y_2O_3 concentration between 4-14 mol%. It was found that Y_2O_3 does not segregate toward the GB core for one of the grain orientations. On the contrary, Y prefers to accumulate in this particular grain after the A&R process. As a result, it allows a better distribution of oxygen vacancies inside the grain interior what leads to obtaining a higher oxygen-ion self-diffusion for this region

A 3D Finite Element Method model designed for nanocolumnar µSOC oxygen electrodes

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With the growing interest in sustainability for the Internet-of-Things (IoT), the miniaturization of Solid Oxide Cells (SOCs) would provide new and greener possibilities for powering portable electronic devices. However, the recent development of micro-Solid Oxide Fuel Cells (µSOFCs) still faces several challenges, and the electrodes and electrolyte composition and microstructure, as well as the microfabrication technology, are still being optimized for enhanced device performance at moderate temperatures. To investigate and optimize efficiently the material performance, electrode microstructure, cell architecture, and device design numerical simulations are often coupled with experimental results.

This work is based on a previous 3D Finite Element Method (FEM) model used for studying macrohomogeneous SOFC cathodes [1]. This model has been extended and adapted to study the architecture of the oxygen electrode of a µSOFC. A simplified geometry is constructed based on SEM and TEM observations. The model includes the oxygen gas diffusion into the electrode pores, the oxygen surface exchange into the material, the bulk ionic diffusion, and the charge transfer at the electrode/electrolyte interface. As a case study, a lanthanum nickelate (La_2NiO4) nanocolumnar electrode (<1µm) grown on a single crystal YSZ substrate is modelled [2]. Based on EIS experimental measurements, the surface exchange coefficient was estimated, while other parameters, such as the diffusion coefficient, the electrode oxygen concentration, and the electrolyte ionic conductivity, were taken from the literature. The 3D FEM model has been validated by experimental results both for the area specific resistance and for the impedance spectra measured as a function of the temperature. Thanks to the model, we have been able to study the influence of the nanocolumn thickness, grain size, gap between nanocolumns, and the thickness of the La_2NiO_4 dense layer on the electrode performance, which will help us design improved architectures in the future. Furthermore, the co-limiting surface exchange and bulk diffusion processes have been investigated to find the optimum nanocolumn thickness.

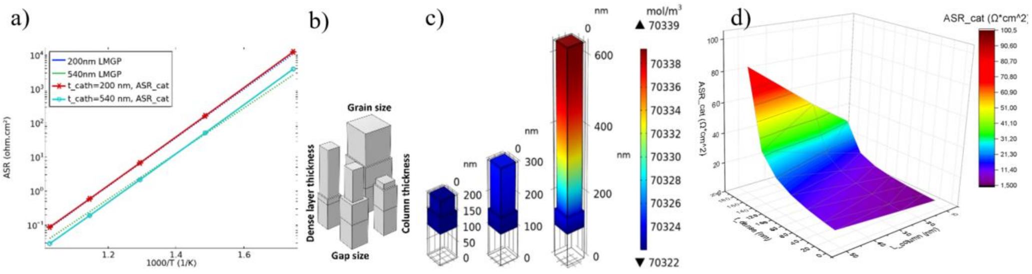

Figure 1: a) Validation of simulated electrode ASR with ASR measured by EIS, b) Four morphological parameters for optimization of the nanocolumn architecture, c) oxygen concentration in 100, 200, and 500 nm thick La_2NiO_4 electrode (at 500 °C), d) impact of dense La_2NiO_4 layer thickness and the grain size on the electrode ASR.

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Evaluation of the stability of PCFC electrodes based on double perovskite cobaltites

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Protonic ceramic fuel cells (PCFCs) enable direct electrochemical conversion of hydrogen to electricity with high energy efficiency and fuel utilisation. Their advantage regarding solid oxide fuel cells (SOFC) is that they produce water on air side electrode avoiding dilution of fuel and reduction of working temperatures (400–600 °C), which improves stack durability. However, the decrease in temperature also affects the catalytic activity of the electrodes, being especially limited in the case of the cathode. Cathode materials suitable for operation at reduced temperature must exhibit high catalytic activity for the oxygen reduction reaction (ORR), and high values of the surface exchange coefficient, while being known as mixed ionic-electronic conductors (MIECs).

Ordered double perovskite cobaltites with the general formula $BaLnCo_2O_{6-\delta}$, (where Ln is a lanthanide or a combination of lanthanides) are promising candidate materials for the air electrodes. By doping the perovskite structure, the local chemical properties may be tailored. The double perovskites can arrange in different symmetries (from cubic Pm-3m, to tetragonal P4/mmm or orthorhombic Pmmm) depending on the ionic radius of the lanthanide and the oxygen content. Thus, the incorporation of water in the lattice, present in the electrode may affect the structure stability or symmetry of the double perovskites.

The effects of water steam on the electrode stability have been assessed for a series of doped $BaLnCo_2O_{6-\delta}$. The materials have been submitted to several tests at temperatures within 200 and 600 ºC and electrode operation water partial pressures, up to 10 bar. XRD measurements before and after exposing double perovskite powders to a series of high water partial pressures and high temperature indicate that the ability to maintain the pristine structure depends on the dopants and the combination of them. Besides, this study sets the possible operation limits of the materials and allows a design strategy for stable materials.

Acknowledgements

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Influence of stochiometric complexity on performance of multi-constituent ceramic protonic conductors

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The so-called High Entropy Oxides (HEOs) constitute a new group of materials consisting of a minimum of five elements randomly occupying one position in the crystal structure and by this stabilize compound by configurational entropy [1]. Recently we reported that for some perovskite HEO show a protonic contribution to conductivity [2]. To follow up we decided to synthesize and analyze the wider group of high entropy proton conductors: perovskite HEO based on barium zirconate. For such structures, the energetics of formation can be exceptionally interesting, especially in comparison to low entropy equivalents. We employed multiple techniques including X-ray diffraction, thermogravimetry, impedance spectrometry, and electrochemical relaxation techniques as well as high temperature oxide melt solution calorimetry [3] for the determination of complex properties of this system. This talk will summarize our findings and address whether such high entropy materials are suitable for future applications in PCECs.

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Redox-stable electrodes for CH_4 conversion in proton ceramic cells

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Electrochemical reactors with proton-conducting ceramic electrochemical cells create the opportunity to intensify the hydrocarbons conversion processes via the in-situ H_2 extraction of the produced. However, these non-oxidative operation conditions are prone to produce coke, which provokes the catalyst deactivation and loss of the electrode performance. Therefore, an oxidative regeneration cycle is required to restore the catalyst activity.

In this work, different composite materials are investigated as redox-stable electrode backbones for their integration in proton ceramic cells, based on $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ (BCZY27) and $La_{0.85}Sr_{0.15}FeO_3$ (LSF8515), $La_{0.5}Sr_{0.5}FeO_3$ (LSF55), $La_{0.84}Sr_{0.16}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) or $La_{0.8}Sr_{0.2}MnO_3$ (LSM). An alternative method to improve the performance is also suggested by catalytically activating the electrode surface. Chemical and structural compatibility, detailed electrochemical impedance spectroscopy and stability in redox cycling will be discussed in the 500-800 ºC range, showing LSCM and LSM as high potential electrodes for non-oxidative hydrocarbon upgrading and redox-regenerative cycling.

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Towards better oxygen electrodes for r-µSOC:

Investigation of LSC and LSM based VAN electrodes under bias.

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Solid oxide cells (SOCs) are electrochemical devices with the capability of reversibly converting chemical energy to electricity. Considering the developments in the thin film technologies, thin film based SOCs could potentially use new nano-engineering concepts to improve their performance. However, one of the limitations of these devices remains the sluggish electrode catalytic activity and their long-term stability. State of the art nanofabrication strategies are being used/developed to further enhance the performance of the mixed ionic and electronic conductors, which are materials used for the oxygen electrode. Some of these strategies include strain engineering[1], chemical doping[2], surface decoration[3] etc.

Another, extremely promising nanoingineering approach, is the fabrication of electrodes based on vertically aligned nanstructures (VANs), which can be described as nanoscale alternating phases extruding perpendicular to the substrate in which they were grown. In this work, we present electrochemical characterization of VAN nanocomposite electrodes, under anodic and cathodic bias as well as a comparative study with their constituent phases. Two different VAN based air electrodes were studied in this work. The first being composed of a mainly electronic conductor $La_{0.8}Sr_{0.2}MnO_3$ and an ionic conductor $Ce_{0.8}Sm_{0.2}O_2$ (LSM/SDC) and the second, composed of a MIEC, $LaSr_{0.2}Co_{0.8}O_3$ and $Ce_{0.8}Sm_{0.2}O_2$ (LSC/SDC). All samples investigated in this work were grown by pulsed laser depositions on 8YSZ (100) substrates.

The VAN based electrodes show better thermal stability at elevated temperatures, and in the case of LSM/SDC improved surface resistance[4]. Therefore, we have investigated them under bias, with the purpose of comprehending their potential as air electrodes in r-µSOC. The LSC/SDC VAN electrode exhibits enhanced performance under anodic bias when compared to LSC, making it a good candidate for electrolysis and reversible cells. Additionally the chemical capacitance obtained from the electrochemical impedance measurements; give some incentive on the defect chemistry of these electrode materials.

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Enhancing SOC cathode performance using tailored nano-columnar $La_2NiO_{4+\delta}$ thin films

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Physicochemical processes are at the basis for the operation of electrochemical devices such as solid oxide cells, with the oxygen reduction reaction being among the most relevant ones. High oxygen exchange activity is therefore essential and its optimisation is the goal of various research strategies by tuning the intrinsic and apparent activity.

In this study, we have selected $La_2NiO_{4+\delta}$ (L2NO4), a very promising cathode material for intermediate and low temperature solid oxide cell applications, due to its good electronic and ionic conductivity, together with its high oxygen exchange activity with a low activation energy. Oxygen incorporation and transport in $La_2NiO_{4+\delta}$ thin films is limited by surface reactions. Hence, tailoring the surface morphology is expected to lead to an overall improvement of the electrode performance.

We show how to tune the apparent and intrinsic activity of La_2NiO_4 thin films by tailoring their nano-structure using Pulsed Injection Metal Organic Vapour Deposition (PI-MOCVD). We were able to tune the morphology of the films, achieving a nano-columnar microstructure, with open porosity and a significantly enlarged specific surface area and therefore found a remarkably enhanced surface activity by electrical and electrochemical analysis. We found that this nano-columnar structure is rooted in a dense bottom layer, serving as good electronic and ionic conduction pathway.

While the larger surface area plays an important role in the observed enhancement, it does not account for the total activity increase. Hence, we will also discuss intrinsic activity improvements, likely caused by different terminations and nano-features, observed on the lateral side of the nano-columns, such as kinks and edges, leading to a surface with distinct, faster exchange coefficients.

Overall, the growth of nano-architectured La_2NiO_4 thin film cathodes by PI-MOCVD resulted in a substantial enhancement of the oxygen exchange activity and opens up a new route towards the optimisation of electrode materials for intermediate to low temperature devices.

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Hybrid oxide superlattices as electrocatalysts for the oxygen evolution reaction in alkaline electrolyte

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Due to their tunability concerning the individual A- and B- site cations perovskites are an interesting material for the oxygen evolution reaction. Stable materials are mostly less active and active materials are not stable. This inverse relationship between activity and stability was tried to overcome by fabricating unit cell precise superlattices.

The active but considerably unstable perovskite $La_{0.6}Sr_{0.4}CoO_3$ was used as a benchmark thin film catalyst and tried to be optimized using an artificially designed superlattice structure. Therefore, $SrTiO_3$ as a stable but inactive perovskite was introduced and combined with $La_{0.6}Sr_{0.4}CoO_3$ via superlattice structure. Two types of superlattices were synthesized, which can be distinguished by their surface layer: (1) $SrTiO_3$-terminated, and (2) $La_{0.6}Sr_{0.4}CoO_3$-terminated surface.

The measured lifetime of the $SrTiO_3$-terminated superlattices exceeded the reference lifetime of the bare $La_{0.6}Sr_{0.4}CoO_3$ by multiple hours. It was found that 17 internal interfaces gave the highest recorded lifetime of 27 h under static load of 5 mA/cm$_2$, which is an improvement by 17 h (170% increase) compared to the single layer $La_{0.6}Sr_{0.4}CoO_3$ catalyst (10 h). The higher stability led to a decreased activity, which is observed by the increased overpotential of 100 mV.

The post-mortem superlattices showed degradation on the surface but maintained the superlattice like features in the bulk, visible through x-ray diffraction analysis. These results suggest that the introduction of superlattice structure in the catalysts can lead to an improved structural and electrochemical stability and is an exciting approach to make water electrolysis more efficient and therefore economically feasible in the future.

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