PE00000021
“PNRR MUR - M4C2 – NEST - Extended Partnership Network 4 Energy Sustainable Transition”

SPOKE N. 4

CUP D33C22001330002

Research proposal

Topic addressed by the project
(with reference to Allegato 2)

DIONS – Design of an Innovative Dual-ion conduction Solid Oxide Cell for the co-electrolysis of H₂O and CO₂ at intermediate temperatures.

- University of Udine
- Marta Boaro
- Proposal duration in months: 12 months
- Marta Boaro, associate professor (PI)
- Carla de Leitenburg, associate (co-PI)
- Name and qualification of the components the research team

<table>
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<th>ROLE IN THE PROJECT</th>
<th>NAME</th>
<th>SURNAME</th>
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<th>QUALIFICATION</th>
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<td>Principal Investigator</td>
<td>Marta</td>
<td>Boaro</td>
<td>University of Udine/Polytechnic Department of Engineering and Architecture</td>
<td>Associate Professor</td>
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<td>co-Principal Investigator (PI)</td>
<td>Carla</td>
<td>de Leitenburg</td>
<td>University of Udine/Polytechnic Department of Engineering and Architecture</td>
<td>Associate Professor</td>
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ABSTRACT

“DIONS” project is in line with the first theme of research of this call (WP 4.1.1 “Innovation for Fuel Cells and Solide Oxides), the PNRR 2021-2027 directives, and Europe's Green Deal and H₂ EU strategy for a carbon-neutral economy. Its main goal is the valorisation of non fossil CO₂ streams by direct co-electrolysis of CO₂ and water to added value products, namely syngas, using Solid Oxide Electrolysis Cells (SOEC) with mixed protonic and anionic conduction. The double ionic conduction would decrease the high operating temperature (700-900 °C) of traditional solid oxide electrolysis cells (SOECs) up to 500-600 °C, allowing the co-electrolysis of H₂O and CO₂ at intermediate temperature. This helps the thermal integration with downstream chemical syntheses and the OPEX cost of co-electrolyser due to degradation of materials. The novel aspects of this technology include the separation of steam and CO₂ within the cell, eliminating the need for steam compartment compression, selective pressurisation of the syngas compartment and the production of dry hydrogen. In particular, the project will explore the modulation of the mixed protonic-anionic electrolyte conductivity, opening up new possibilities for combining co-electrolysis with the Reverse Water Gas Shift (RWGS) reaction, thereby advancing CO₂ valorisation efforts. The lower operating temperature requires the development of more active materials and specialised device architectures. "DIONS" addresses this challenge through optimised synthesis of electroceramic materials, comprehensive characterisation of their electrochemical, chemical and catalytic properties and laboratory-scale implementation of SOEC for CO₂/H₂O co-electrolysis. By striking a balance between experimental work on SOECs and in-depth analysis of electrochemical/chemical processes, the project aims to unlock the full potential of its innovative approach to CO₂ valorisation.
RESEARCH PROPOSAL

Section a. State-of-the-art and objectives

In pursuit of aligning with National and European set-plans aimed at significant reductions in CO₂ emissions and improvements in energy efficiency, it becomes imperative to explore and implement environmentally sustainable processes. These processes must effectively manage the intermittency of renewable resources while meeting the energy demands of consumers. Among the many enabling technologies, Solid Oxide Electrochemical technologies have emerged as promising solutions due to their ability to efficiently generate and store electricity. These technologies, including fuel cells (SOFCs), electrolyzers (SOECs), and reverse fuel cells (R-SOFCs), play a critical role in establishing robust power-to-X chains that rely on renewable energy sources. [1, 2].

The SOEC operates at high temperature (HT) (750°C-900°C) more efficiently than a PEM electrolyser with the unique ability to simultaneously convert carbon dioxide and water (co-electrolysis process) into syngas, which can then be converted into high density fuels through specific downstream chemical processes. Over the past 15 years, the technology has undergone tremendous development, with single cell and stack performance doubling and durability improving by a factor of 100 [1]. This makes high temperature co-electrolysis currently the best approach to recycle CO₂ at a suitable reaction rate under appropriate thermodynamic conversion conditions to achieve a suitable yield of syngas [1, 3]. Despite several advances, (HT)-SOECs still face a number of challenges, mainly due to their operating temperature, before reaching market readiness; in particular i) poor dynamic behaviour, ii) modest tolerance to redox and thermal cycling, limited lifetime and poor tolerance to trace impurities (sulphur, silicon, etc.) [4, 5]. Intermediate temperature (IT) operation (500°C-600°C) can in principle reduce all these drawbacks. In particular, it will benefit the dynamic operation as required for coupling with renewable energies, and facilitate integration of the SOEC with downstream exothermic processes for the conversion of syngas into fuels. Moreover, costs will be saved due to cheaper materials for balance of plant equipment, smaller heat exchangers and minor insulation requirement.

Proton conductor oxide cells (PCOCs) have recently emerged as a new type of SOEC for the production of chemical fuels, [6,7] and methane [8]. PCOCs are based on proton-conducting ceramic electrolytes which transport protons (H⁺) from the water vapour anode to the hydrogen cathode with lower migration barrier than oxide ions, making them suitable for operation at intermediate temperatures (400 to 650°C). This offers advantages in the development of integrated Power-to-X chains of decarbonisation chains, as these temperatures are closer to those of renewable heat sources (solar thermal, geothermal), industrial waste heat and downstream chemical processes. Despite this advantage, electrolysis with PCOCs is lagging behind HT-SOECs in development (TRL3 to 4) and requires further studies on materials and systems for its scale-up [9].

An effective approach to the development of an IT-SOEC co-electrolyzer can be drawn from recent advances in proton conductors (PCs), which have shown dual ionic conductivity (oxygen anions and protons) under certain conditions, facilitating SOEC operation [10-15]. Recent and efforts have focused on the development of proton conducting oxides (PCOs) based on barium zirconates (BZOs) and barium cerates (BCOs) to improve their chemical stability and proton conductivity [16-19]. Aliovalent-doped BaCeₓ₋ₓZrₓO₃₋ₓ (BCZ) has shown promising results in terms of high proton conductivity and overcoming problems such as poor sintering and low proton conductivity of single BZ-BC oxides [20]. Due to the presence of oxygen vacancies, cerate and zirconate perovskite, possibly doped with yttrium to improve carbonation resistance, exhibit both proton and oxygen-ion conduction [21], which is advantageous for the co-electrolysis of H₂O and CO₂ at intermediate temperatures. Protons are much more mobile than oxygen ions at low temperatures, while the concomitant oxygen-ions conduction would allow the co-electrolysis of H₂O and CO₂. Tuning the conductivity of protons and oxygen ions is crucial to achieve co-electrolysis at low temperatures.

On the other hand, research is being carried out to study and exploit the electronic properties of the heterointerfaces of oxide composites [21, 22] for the implementation of materials with advanced properties potentially capable of promoting the direct co-electrolysis of CO₂ and H₂O in PCOCs at 400 to 650°C operating temperature [23-27]. Previous studies have shown that the combination of ceria-based fluorites (anionic
conductors) and perovskite oxides (proton conductors) is a promising approach to modulate the mechanical and electronic properties of the resulting composite via the interfacial properties \[28,29\], and could be a shortcut to develop low-cost electrolytes and electrocatalysts with dual (proton and anionic) or triple (proton-anionic and electronic) conduction, respectively \[30, 31\]. Clearly, the advantages of composite materials over the design of a single-phase double-ionic conductor are: i) easier control of the transfer numbers of charged species, ii) conductivity results less dependent on operating conditions, iii) suppression of the internal short-circuit due to the electronic conductivity of the individual phases, iv) improvement of the sintering capability, v) better control of thermal, redox and environmental stresses occurring in operating conditions. However, several challenges remain, such as the assessment of the mechanical, thermal and chemical stability of the fluorite/perovskite phases, the understanding of interfacial and surface interactions, and electrode materials specifically designed for SOEC dual-ion electrolytes. In addition, precise control of the microstructure and composition of the composite will be required to achieve optimum conductivity. The project adopts the strategy of realising dual-ion conduction through the realisation of perovskite/fluorite composites. This can be achieved by preparing composites in which an oxygen ion conducting phase is added to the BCZY perovskite. BCZY-GDC (gadolinium doped ceria) and BCZY-SDC (samarium doped ceria) are used as mixed proton-anionic electrolyte conductors in the proposed system. This proposal focused on simplifying the design of the SOEC cell based on dual ionic conductors, understanding the complex structure/mechanism of the fluorite/perovskite interface, and studying the electrochemical and catalytic processes at the electrodes to demonstrate the feasibility of an innovative co-electrolyser.

Exploiting this approach, we aims to realize a hybrid SOEC [13] for the co-electrolysis of H$_2$O and CO$_2$ to syngas at temperatures of 500-600°C. according to the schematic representation of the figure below.

Principle of hybrid co-electrolyser conceived in this project

Compared to the conventional HT-SOEC, the double ionic conductivity reshapes the reaction system, particularly at the cathode, allowing H$_2$ to be produced electrochemically without the introduction of water. This opens up new possibilities for combining co-electrolysis and reverse water gas shift reaction on the cathodic side of the cell with higher efficiency. Additionally, dual-ionic and electronic conduction can trigger competing reaction paths, potentially mitigating degradation impacts or enabling control over process selectivity under specific operational conditions. This could facilitate the selective production of green-methane over syngas, paving the way for a direct use of the device in the upgrading of biogas to biomethane. Advantages of this proposed technology over conventional SOEC include separation of steam and CO$_2$ on different sides of the cell, elimination of the need to compress the steam compartment, selective pressurisation of the syngas compartment and production of dry syngas. This innovative approach holds great promise for advancing CO$_2$ valorisation and represents a unique direction for next generation co-electrolysis systems. Therefore, the main objective of this project is to develop a novel solid oxide co-electrolysis cell for the direct conversion of CO$_2$ to H$_2$O based on dual ionic (proton-anion) conducting electrolytes and novel electrodes. The co-electrolyzer designed in this proposal will operate at a lower temperature (500-600°C vs. 750-900°C), taking advantage of the mixed-ionic and multi-conducting nature of its components. The aim is to improve the dynamic behaviour, durability and integrability with the downstream syngas conversion processes as well as the CAPEX and OPEX costs of the current SOEC technology in order to widen its exploitation.
Section b. Methodology

The development of project will be articulated in three phase:

**Phase 1 (1M)-Literature survey:** analysis of the technological challenge to be faced, its complexities and the state of the art of currently existing technologies/approaches in order to identify the level of innovation of the proposed solution and of its impact on the development of a carbon neutral economy based on renewable resources.

**Phase 2 (2-10)-Innovation development:** the design co-ionic conduction solid oxide co-electrolyser with improved performance, flexibility and stability, will be obtained through a series of specific objectives and actions, summarized as follows:

1. Synthesis and characterization of the proton conductor oxide (PCO) electrolyte, realization and characterization of the composite electrolyte
2. Synthesis and characterization of the materials and electrode electrocatalysts.
3. Study of the catalytic properties of the fuel electrode in ex-situ condition
4. Electrochemical characterization of electrolyte supported half cells

**Phase 3 (11-12M)-Prototyping and testing:** realization of electrolyte supported single cells and their electrochemical characterization in different conditions (temperatures, gas compositions and concentrations). This phase may needs specific consultancies for manufacturing optimization and accelerating the analysis of EIS results.

The following describes how to implement the proposed innovation (Phase 2)

1. **Synthesis and characterization of the PCO electrolyte, realization and characterization of the composite electrolyte**

   While the fluorite will be purchased from commercially available suppliers, the PCO will be synthetized starting from Ba(Ce,Zr,)O₃ precursors through Modified Pechini Method (MPM). Composites will be prepared by ball milling.

   PC composition will be adjusted through (i) A site doping by low amount of Ca and Sr, to tailor the protonic conductivity due to their suitable ionic radii and basicity, maintaining the carbonation resistance of the perovskites; and/or (ii) B site co-doping by Y, Gd and/or Sm into Ba(Ce,Zr)O₃ perovskite being known that these trivalent ions promote the oxygen vacancy creation and therefore the hydration reaction, i.e. protonic conductivity [14, 15, 32]. PC perovskite and composite between the PC perovskites and (Ce,Sm,Gd,Y)O₂ fluorites will be studied to optimize co-ionic transport and mechanical and chemical stability at 500–600°C to obtain co-electrolysis. The PC materials and the perovskite/fluorite composites will be characterized in their chemical-physical and electronic properties with a multi analytical approach to optimize the best formulation in terms of conduction, mechanical and chemical resistance in the 500–600°C range.

2. **Synthesis and characterization of the materials and electrode electrocatalysts of the SOEC.**

   The synthesis of highly active and redox-resistant catalysts is crucial for addressing operating condition constraints (slow kinetics, mechanical and thermal strains) [1]. Investigation and functionalization of the three-phase boundary and electrode surface are key to optimizing cell design, particularly porous/dense/porous electrolyte layers filled with appropriate electrocatalysts [33, 34, 35]. Optimizing porous nanocomposite layers with triple ion-electron conductivity (TIEC) and multifunctional interfaces is a major project challenge. The deposition of porous layer will be obtained by screen printing. Electrode materials selection is another critical aspect of the electrode realization process.

   The cathode materials suggested in this project are metal (Fe, Co, Cu, Zn, Ni also as mixed oxides or alloys) catalysts for RWGS [36] supported on ceria based oxide. Perovskite/Fluorite electrolyte and its single
components will be used as bench support since their composition is able to promote CO\textsubscript{2} adsorption and activation and avoid formation of carbon [37].

The anodic side of the cell promotes oxygen evolution from water vapor, a typically sluggish reaction that can control overall cell kinetics and cause mechanical stresses and electrode detachment. Mechanisms such as limited ionic conductivity and electrode fragmentation into nanoparticles are common issues. These challenges can be addressed by creating a robust, fast ionic electrode architecture and using highly ionic conductive electrocatalytic materials.

Double perovskites, such as AA'B\textsubscript{2}O\textsubscript{5+δ}, have attracted attention due to their high electrical conductivity and electrochemical activity towards oxygen reactions. SmBaCo\textsubscript{2}O\textsubscript{5+δ}, synthesised with varying amounts of Ca replacing Ba in the A' site, will be studied as an oxygen electrocatalyst [38, 39]. Partial substitution of Co with Cu in the B sites will also be considered to reduce critical raw material usage. BSCF, a well-studied mixed ionic electronic conducting (MIEC) material, will be adopted as a benchmark material, doped with Zr or Zn to improve structural stability at low temperatures [40, 41].

Extensive ex-situ physicochemical, structural and functional characterisation will be carried out using techniques such as XRD, DTA-DSC, TPO, TPR, physisorption of N\textsubscript{2} (BET), SEM, ICP, EDX, Raman and TPO. These analyses cover structural information, thermal properties, surface area, morphology, elemental analysis, interdiffusion phenomena and carbon analysis. In-situ temperature-programmed analyses by XRD, Raman and DRIFT will complement the ex-situ characterisation to understand component interactions, thermal evolution and electrode phenomena under different reaction atmospheres. XPS and HRTEM are used where appropriate to analyse surface composition and to gain insight at the nanoscale.

3. Study of the catalytic properties of the fuel electrode in ex-situ condition

Study of fuel electrode catalytic properties will involve ex-situ screening of formulations through catalytic studies, focusing on the reverse water gas shift and methanation reactions. Promising formulations will be selected for complete cell fabrication with chosen electrolytes and perovskite anodes. Ex-situ catalytic testing will assess electrochemical and catalytic processes interplay at the cathode, utilizing a bed microreactor for kinetics studies. This work aims to understand temperature, gas hourly space velocity (GHSV), and H\textsubscript{2}/H\textsubscript{2}O/CO\textsubscript{2} ratio influences on catalytic activity, selectivity, and poisoning phenomena. Results will be compared with complete cell configuration tests to identify possible synergies between catalytic and electrochemical processes and finally better understand the cathodic processes.

4. Electrochemical characterization of electrolyte supported half cells

Half-cells offer an effective configuration for separately studying electrolytes and electrodes. Electrolyte-supported half cells will be prepared by cold pressing single PCO or composite electrolytes with varying BZCY/GDC ratios. Preliminary studies will utilize half cells with electrodes directly deposited by slurry coating. Following completion of electrochemical characterization, selected composite electrolytes and promising electrodes will be incorporated into electrolyte-supporting half-cells, utilizing a porous layer/electrolyte scaffold. The infiltration of electrocatalysts will be achieved using a precursors solution via auto-combustion. This approach enables microstructure tuning while maintaining a large surface area to potentially enhance electrode performance [35]. Achieving nano-sized dispersion of the electrocatalyst within the porous electrolyte scaffold is a desired outcome to improve both electrocatalytic activity and electrode robustness. Electrochemical characterization will encompass Impedance Spectroscopy (EIS) analysis, cyclic voltammetry, I-V curves, and galvanostatic aging, with temperature, gas partial pressure, and overpotentials being key parameters modulated to gain comprehensive insights into electrode electrochemical behaviour.

References
9. L.Q. Le, et al., J. Power Sources 2021, 482, art. 228868
12. C. Duan, J. Huang, et.al.,, Appl. Phys. Rev. 2020, 7, 011314
13. J. Kim, et al., Nano Energy, 2018, 44, 121-126,
17. V. P. Gorelov, V. B. Balakireva, et al., Russian J. Electrochem., 2010, 46, 890-895. BZ
27. Y. Zhang et.al., Nano-Micro Lett. 2020, 12,178
Section c. Available instrumentations and resources

The laboratories of the group of heterogeneous catalysis of the Polytechnic Department of Engineering and Architecture of UNIUD are equipped with the following:

- Memmert kiln (max T 150°C)
- Furnaces (Lenton UAF 16/5, max T 1500°C; De Marco mod. 10A 10800C, max T 500°C)
- Lenton tubular furnace for heat treatment in reactive atmosphere (max T 1400°C)
- Carbolite Tubular Furnaces (MTF 12/25, CTF 12/75/700 max T 1100°C) for heat treatment under controlled atmosphere
- Rotavapor Büchi R200
- Vibromill Fritsch Pulverisette 23
- Vibromill Retsch MM 500 nano
- Fritsch Pulverisette 2 mortar mill
- Centrifuge Hettich Rotina 380
- Autoclave Parr 4843
- Horiba X'Plora plus Raman microscope equipped with Linkam CCR1000 heated reaction cell
- FTIR Spectrophotometer Thermo Scientific Nicolet iS-50 with heated reaction cell Pike Technologies Diffus'IR
- Micromeritics Tristar porosimeter
- Micromeritics Autochem II analyser, coupled with Pfeiffer Vacuum Omnistar mass spectrometer
- PANalytical Epsilon 5 X-ray fluorometer
- Philips X'Pert diffractometer with Anton Paar reaction chamber
- Thermogravimetry (TGA) TA Instruments Q500
- Thermogravimetry (TGA) TA Instruments 5500 Discovery series
- Differential Scan Calorimetry (SDT) TA Instruments Q600
- Low flow rate oxidation/reduction test plant (60-200 ml/min) consisting of Lenton LTF 12/25/250 tube furnace, Brooks flow regulators (5-200 ml/min), ABB Advance Optima AO2020 gas analyser (CO₂, CO, CH₄, O₂, H₂), Waters 515 HPLC pump, AGT MAK 10 gas condenser, FALC Instruments heating bands.
- CO₂ reduction test plant with low flow rates (60-200 ml/min) consisting of Lenton LTF 12/25/250 tube furnace, Brooks flow regulators (5-200 ml/min), Varian CP4900 two-column micro gas chromatograph, AGT MAK 10 gas condenser, FALC Instruments heating bands.
- Ammonia decomposition test plant consisting of Carbolite MTF 10/15/130 tubular oven, Brooks flow regulators (100-200 ml/min), two-column Varian CP4900 micro-gas chromatograph
- High flow rate adsorption/desorption test plant (300-400 ml/min) consisting of Carbolite VST 12/40/200 tubular oven, Brooks flow regulators (50-500 ml/min), MKS Multigas 2030 gas analyser, ABB Advance SCC-C gas condenser, TEAC and FALC Instruments heating bands.
• High-flow oxidation/reduction test plant (300-400 ml/min) with Elite TSVH12/30/205 tubular furnace, Bronkhorst flowmeters, MKS Multigas 2030 gas analyser, ABB Advance SCC-C gas condenser, TEAC and FALC Instruments heating bands.
• Fuel cell system with Whatman 75-34-220-V452 hydrogenator, Lenton tube furnace (Tmax = 1200 °C, L = 40 cm), 4 Brooks flowmeters + 1 control box, Amel 7050 potentiostat, Amel 7200 frequency response analyser, Material Mates cell test station control panel, Cell furnace, 3 panel mounted M+W instruments flowmeters
• - Mini Tape Casting table for fuel cell preparation.
• Reforming Plant with Tersid Tubular Furnace (Tmax = 1200 °C, L = 30 cm), 8 Brooks flowmeters (max flow rate 100 mL)+ 2 control boxes, 1 pressure gauge SMC ZSE30, GC Agilent 8860 - with columns Carboxen 1000 (H2, CO, CO2, CH4, N2 - carrier He) and ShinCarbon ST 100/120 (H2 - carrier N2)
• Chemical looping plant with Carbolite Gero tubular furnace (Tmax = 1000 °C, L = 15 cm) 4 Brooks flowmeters + control box, 2 SMC ZSE20 pressure gauges and Hiden HPR20 mass spectrometer
• Thermo photo catalysis system on panel with 5 Gas Lines, 5 Mass Flow Controllers of which 4 Bronkhorst: 3 with remote control, 1 with manual control; 1 Brooks Mass Flow Controller driven with 0-10V analogue signal, Solenoid Valves, Evaporator, Modular I/O System: ADAM-5000 Series - Advantech for acquisitions, Band heaters with mineral insulation, sheath material Stainless Steel, max operating temperature 760°C, power 1200W, Arduino Uno for driving furnace resistor and TC acquisition, Customized reactor with quartz window, “custom-made” bench control software programmed in LabView 2018 environment, Balzers FL-9496 mass spectrometer , QUADSTAR 422 V 5. 04 software, QMS 200.

Section d. GANTT diagram

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Section e. Milestones, Deliverables and KPI

Milestones and KPIs
M 1 Synthesis of electrolyte with conductivity @550°C comparable with traditional SOEC @700°C (4M)
M 2 Identification of fuel electrode components, selectivity in syngas >80% @ 600°C (7M)
M 3 Realization of fuel and oxygen electrode half cells (10M) with resistance lower than 0,03 ohm cm²@ 600°C (10M)
M 4 Realization of a full electrolyte supported cell, - electrochemical cell performances better than 0.85 A cm² at 1.4 V at 500-600°C (12M)
Deliverables
D 1 Report on literature survey (1M)
D 2 Report on synthesis and characterization of materials (8M)
D 3 Final report with results of electrochemical characterization (12M)

Annexes: Curriculum vitae research team
Appendice dell’Allegato B

Curriculum vitae PI or CO-PI

PERSONAL INFORMATION
Family name, First name: de Leitenburg Carla
Researcher unique identifier(s):
Scopus Author ID: 6701455796
ResearcherID: P-4796-2015
orcid.org/0000-0003-2226-574X

Date of birth: 
Nationality: 
URL for web site: https://catalysis.uniud.it/the-group/carla-de-leitenburg

EDUCATION
1994  PhD Chemical Sciences
Department of Chemistry, University of Trieste, Italy
Prof. Mauro Graziani
1989  Master Chemistry
Department of Chemistry, University of Trieste, Italy

CURRENT POSITION(S)
2000 – 2024  Associate Professor of Industrial Chemistry
Polytechnic Department of Engineering and Architecture of the University of Udine, Italy

PREVIOUS POSITIONS
1993 – 2000  Researcher of Industrial Chemistry
Engineering Faculty, Department of Chemical Sciences and Technologies of the University of Udine, Italy

FELLOWSHIPS AND AWARDS
SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS

2010 – 2024 4 PhD/ 3 Bachelor Students
Polytechnic Department of Engineering and Architecture, Udine University, Italy

ORGANISATION OF SCIENTIFIC MEETINGS

2012 Organizing committee 8th International Conference on f-Elements 350 participants
(Udine, Italy)
2014 Organizing committee Workshop Fundamentals and applications of cerium dioxide in catalysis, 100 participants (Udine, Italy)

INSTITUTIONAL RESPONSIBILITIES

1993 – 2016 Engineering Faculty member, Udine University Italy
2000 – 2003 Member “Commissione Interna per il Tutorato e l'Orientamento” Engineering Faculty, Udine University Italy; president (2001 – 2003)
2000 – 2003 Member “Commissione d’Ateneo per il Tutorato e l'Orientamento” Udine University, Italy.
1999 – 2000 Member of the Enlarged Academic Senate (Rep of Researchers); Udine University, Italy
2009 – 2010 Member of Department of Chemical Sciences and Technologies Board, Udine University, Italy
2009 – 2012 Member of Engineering Faculty Board, Udine University, Italy
2017 – 2020 Member of Engineering Faculty Board, Udine University, Italy

Current Teaching Activities
2022 – 2024 Fundamentals of processes treatment of air pollutants Bachelor’s Course “Industrial Engineering for Environmental Sustainability” Polytechnic Department of Engineering and Architecture, University of Udine, Italy
2020 - 2024 Processes for Energy and the Environment: Master’s Course “Management Engineering (Environmental Sustainability)” Polytechnic Department of Engineering and Architecture, University of Udine, Italy
2023 -2024 Fundamentals of chemical industry processes: Master’s Course “Sustainable Environmental Science and Technology” Department of Agricultural, Environmental and Animal Science, University of Udine, Italy

REVIEWING ACTIVITIES

2000–2024 Reviewer of several catalysis journal, Polytechnic Department of Engineering and Architecture, Udine University Italy

MEMBERSHIPS OF SCIENTIFIC SOCIETIES
2010 –2024 Associated Member “Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali”, Name of Faculty/ Department/Centre, Name of University/ Institution/ Country

MAJOR COLLABORATIONS

Prof. Jordi Llorca, Institute of Energy Technologies, Department of Chemical Engineering and Barcelona Research Centre in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
Dr. Luciana Lisi, Istituto di Ricerche sulla Combustione IRC-CNR, Napoli, Italy

RESEARCH INTERESTS:
Main scientific interest: in synthesis, characterization and testing of heterogeneous catalysts with particular attention to materials containing rare earths with high oxygen storage capacity for applications in the catalytic reaction of environmental implications. Focus on redox reactions for treatment of exhaust gases from diesel, gasoline engines, production of hydrogen and carbon dioxide activation.

The main research projects in which she participated with various national public research institutions are: 40% 98 (Catalizzatori innovativi di combustione per applicazioni energetiche, Coordinatore Prof. P. Forzatti, unità operativa di Udine), Prin 2001 (Catalizzatori ad elevata attività per combustione di metano in condizioni magre, Coordinatore Prof. P. Forzatti, unità operativa di Udine), Prin 2002 (Catalizzatori innovativi per la produzione di idrogeno da idrocarburi leggeri per l'alimentazione di celle a combustibile, Coordinatore Prof. V. Specchia, unità operativa di Udine), Prin 2003 (Sintesi e caratterizzazione di catalizzatori redox per la combustione di particolato, Coordinatore Prof. P. Ciambelli, unità operativa di Udine), Prin 2004 (Catalizzatori innovativi di “water gas shift” a base di ossido di cerio per la produzione di idrogeno per celle a combustibile a membrana polimerica: analisi cinetica e del meccanismo di reazione, Coordinatore Prof. V. Specchia, unità operativa di Udine), FISR 2003 (Programma strategico “Nuovi sistemi di produzione e gestione dell’energia”, Matrici di microcombustori ad idrogeno, Coordinatore dr. P. Perlo), FISR 2005 (Progetto-Obiettivo “Celle a combustibile. Celle a combustibile ad elettroliti polimerici e ceramici: dimostrazione di sistemi e sviluppo di nuovi materiali” Coord. Antonucci), FIRB 2001 (Materiali con caratteristiche redox per l’attivazione ossidativa in condizioni anaerobiche di paraffine leggere, Coordinatore prof. G. Dolcetti), Programma Operativo Interreg IV Italia-Austria 2007-2013 (Nuovi materiali per la rimozione di inquinanti dai gas esausti dei motori a combustione, Responsabile scientifico prof. A. Trovarelli).

Research projects financed by the FVG region G (L.R. 3/98 1999 Catalizzatori Avanzati per Disinquinamento di Reflui Gassosi da Fonti Mobili e Stazionarie, Coordinatore Prof. M. Graziani, e 2002 Materiali ad alta Stabilità Termica e Resistenza all’avvelenamento da Zolfo per il Trattamento Catalitico di Reflui da Processi di Combustione di Origine Civile, Industriale e da Autoavventura, Coordinatore G. Dolcetti; L.R. 11/03 2005 Individuazione e realizzazione di catalizzatori nanostrutturati per la produzione di idrogeno Referente Prof. R. Rosei; L.R. 26/05 art 23 2007 Catalizzatori nanostrutturati per la produzione di idrogeno e sperimentazione pre-industriale Referente Prof. R. Rosei e L.R. 26/05 art 23 2007 Studio dell’abbattimento di contaminanti dell’aria con filtro a base di carbone e allumina attivati ed impregnati Referente Prof. A. Trovarelli).
She participated in industrial research conventions: Treibacher Industrie AG e Frauenthal 2003-2006 (Advanced SCR catalysts I e II) e Treibacher Industrie AG dal 2006 (Mixed Rare Earth /Zr Oxides with Enhanced Thermal Stability and Oxygen Storage Properties I, II e III), Labiotest 2006-2007 (Valutazione dell’efficacia di abbattimento dei contaminanti presenti nell’aria attraverso la filtrazione su carbone e allumina attivati e impregnati con percentuali variabili di reagenti), Umicore, Eni e al Programma Interreg Italia-Austria 2014-2020 Coat4Cata (Sviluppo di rivestimenti e processi di rivestimento per il trattamento catalitico dei gas esausti).

Times cited 7,090, H index 41, 76 articles (Web of Science), 2 contributions to books on Ceria materials (LONDRA: Imperial College Press).

Appendix: All current grants and on-going and submitted grant applications of the PI and Co PI (Funding ID)

Current grants (Please indicate "No funding" when applicable):

<table>
<thead>
<tr>
<th>Project Title</th>
<th>Funding source</th>
<th>Amount (Euros)</th>
<th>Period</th>
<th>Role of the PI</th>
<th>Relation to current proposal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alternative Materials for Emissions control in hybrid vehicle devices (AMELIE)</td>
<td>PRIN</td>
<td>71923</td>
<td>2023-2025</td>
<td>Uniuad coordinator</td>
<td>Development of innovative catalysts and oxygen storage materials</td>
</tr>
</tbody>
</table>
Appendice dell’Allegato B

Curriculum vitae PI

PERSONAL INFORMATION
Family name, First name: Boaro Marta
Researcher unique identifier(s) Orcid ID: http://orcid.org/0000-0002-6853-2965
Date of birth:
Nationality:
URL for web site: https://catalysis.uniud.it/

• EDUCATION

2000 PhD degree in Chemical and Innovative Materials, University of Udine, Department of Chemical Sciences and Technologies, supervisor prof Giuliano Dolcetti

1993 Degree in Chemistry at University of Padova

• CURRENT POSITION

2014 – today Associate Professor in Industrial Chemistry and Technology at University of Udine, Polytechnic Department of Engineering and Architecture, Italy.

• PREVIOUS POSITIONS

2006 – 2014 Researcher at University of Udine, Department of Chemical Sciences and Technologies, Italy

• FELLOWSHIPS AND AWARDS

2004-2006 Post doc position Laboratory of Heterogeneous Catalysis, Department of Chemical Sciences and Technologies, University of Udine, Italy

2001-2003 Postdoc position at the Laboratory of Fuel Cell and Heterogeneous Catalysis (prof. Raymond Gorte), Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia PA, USA

04-07 2000 Young researcher fellowships at the Department of Engineering and of Materials Science, Northwestern University, Evanston, IL, (USA), Lab. Solid State Electrochemistry, supervisor prof. Thomas Mason


• CURRENT RESEARCH INTERESTS:

Fellowships in the USA were very fruitful in developing expertise in solid oxide fuel cells and solid state electrochemistry, while fellowships at the Universities of Udine and Prague in the field of heterogeneous catalysis. Based on these experiences, the research interests have been directed towards studying the relationship between thermo-catalysis and electrocatalysis in electrochemical energy technologies.
More than 20 years of experience in the field of rare earth oxides, their structural and functional characterisation for applications in catalysis and electrochemistry, and more recently in photocatalysis and the development of energy systems for the green production of fuels (H₂, CO₂ valorisation). Currently prof Boaro is responsible of the Laboratory of Fuel Cell and Electrocatalysis in the group of Heterogeneous Catalysis of the Polytechnic Department of Engineering and Architecture of University of Udine, Italy

• **SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS**

2010 – 2024 4 Post Doc/5 PhD University of Udine, Faculty of Engineering, Polytechnic Department of Engineering and Architecture (current name), University of Udine, Italy

• **ORGANISATION OF SCIENTIFIC MEETINGS AND SUMMER SCHOOLS**


2014-2024: Member of Organization/Scientific Board of annual National School SIER (School of Introduction on Renewable Energy Sources, Udine (I-X editions)

July 14-18 2014: Coordinator with prof Antonino Salvatore Aricò of the CISM Course Advanced Professional Training School on Advances in Medium and High Solid Oxide Fuel Cell.

August 26-31 2012: Member of Organization Board 8th International Conference on f-Elements, Udine, Italy (350 participants).

• **INSTITUTIONAL RESPONSIBILITIES**

Former Positions at the Department of Chemistry, Physics and Environment (DCFA), University of Udine, Italy
- Representative of the Researchers in the Junta of the Department

Current and past positions at the Polytechnic Department of Engineering and Architecture (DPIA), University of Udine, Italy
- 2020-current-Delegate of the Erasmus Mobility Program for the Industrial Engineering for Environmental Sustainability, Bachelor's Degree Programme
- 2016-2019- Delegate of the Erasmus Mobility Program for the Engineering for Energy and Environment Master program
- 2014-current member of the Committee of the PhD school of Engineering for Energy and Environment,
- 2019- 2024 DPIA Referent for the European platform ETIP European biofuels technology platform
- 2019-currently representative of Associate Professors in the Junta of DPIA
- April -June 2020 enrolled for the Cooperation with APRE for project plans of Horizon Europe - cluster clime-energy- environment.
Current Teaching Activities, Polytechnic Department of Engineering and Architecture, University of Udine, Italy

- Module in the Bachelor’s Course “Industrial Engineering for Environmental Sustainability” Instrumentation for Industrial Processes Control

- Module in the Master Course “Management Engineering-energy curriculum” Technologies for the reduction of gas- greenhouse and energy storage

- Module in the Master course” Industrial Engineering for Sustainable Manufacturing” H₂ Technologies

- Annual Lectures in the PhD program for Engineering for Energy and Environment (University of Udine): Fundamentals on Heterogeneous Catalysis.

Members of the following Committees of Master/Bachelor Courses, University of Udine, Polytechnic Department of Chemical Engineering, Italy:
Bachelor Program Industrial Engineering for Environmental Sustainability
Master Program Management Engineering-energy curriculum
Master Program Industrial Engineering for Sustainable Manufacturing

• MEMBERSHIPS OF SCIENTIFIC SOCIETIES

2014 –2024  Associated Member “Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali”
2017-2018  Member of The Electrochemical Society (ECS)

• REVIEWING ACTIVITIES

2019 – 2020  Guest Editor for the special issue “Advances in Techniques for Characterization of Non Stoichiometric Oxides and Their Applications,” Catalysts, MDPI publishers,


• MAJOR COLLABORATIONS

• Current Collaboration
Prof. Amed Ghoniem, Massachusetts Technology Institute Mechanical Engineering Department, USA (1 join paper).
Prof. Jordi Llorca – Institut de Tècniques Energètiques and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya (Spain) 17 joint paper published.
Prof. Santarelli Massimo, Polytechnic of Turin, Italy 2 join papers
Prof. Alessandro Donazzi and Prof Gianpiero Groppi – Milan Polytechnic, Italy (started in 2013)- 2 joint papers published
Prof. Lu Xinying (University of South Africa, Johannesburg, Africa), recent exchanges collaboration on Fisher Tropsch Process.
Prof. Fausto Gallucci, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, (NL)
Prof. Antonio Barbucci, University of Genova, Department of Civil Engineering, Chemistry and Environment (Italy)

- **Past collaborations**
  Prof. Arup Gayen Department of Chemistry, Jadavpur University, (India) 2 joint papers published
  Prof Raymond Gorte, Univ. Penn, Dept. Chem. Engin., Philadelphia (USA) 4 joint paper
  Dr. Zdanek Vit ASCR, Inst Chem Proc Fundamentals, Czech Republic, 3 joint paper
  Prof. Elisa Garcia-Lopez, University of Palermo, (Italy), 1 joint paper
  Dr. Armelao Lidia, 3 joint paper, and Prof. Antonella Glisenti, University of Padova (Italy), (2 join paper),
  Prof. Patrizia Fronterra (3 join paper), prof. Antonino Aricò, (PRIN 2017), prof. Bangjiao Ye, University of Science and Technology of China, State Key Laboratory of Particle Detection and Electronics, , Hefei (People’s Republic of China), 1 joint paper,

- **SCIENTIFIC PUBLICATIONS:**
  Author or coauthor of 72 scientific publications in top international journals and more than 50 contributions to International or National Congress, she is co-authors also of four book chapters on the application of ceria oxide in heterogeneous catalysis for energy and environment application (Elsevier, Nova Publishing, Imperial College Press, Springer) and co-editor of a book entitled “Advances in Medium and High Temperature Solid Oxide Fuel Cell Technology” (CISM- Springer).

- **Scientometric indexes (2024)**
  Prof. Boaro’s publications have received 4521 citations and she has an h-index of 27 in Scopus.

- **Distinctions**
  2012 by Chemical Italian Society, Poster Award GIG2012, for the quality of research in catalysis for the environment and the energy.

- **Publication inherent to the project**
Boaro M., Mortalo C., Rebollo E., Zin V., Aneggi E., Fabrizio M., et al. Insights on the interfacial processes involved in the mechanical and redox stability of the BaCe$_{0.65}$Zr$_{0.20}$Y$_{0.15}$O$_{3-\delta}$–Ce$_{0.85}$Gd$_{0.15}$O$_{2-\delta}$ composite. ACS Appl. Ener. Mat. 2020; 3, 9877-9888

Mortalò, C., Santoru, A., Pistidda, C., Rebollo, E., Boaro, M., Leonelli, C., Fabrizio, M. Structural evolution of BaCe$_{0.65}$Zr$_{0.20}$Y$_{0.15}$O$_{3-\delta}$–Ce$_{0.85}$Gd$_{0.15}$O$_{2-\delta}$ composite MPEC membrane by in-situ synchrotron XRD analyses, Mater. Today Energy, 2019, 13, 331-341.

Luisetto, I., Tuti, S., Romano, C., Boaro, M., Di Bartolomeo, E., Dry reforming of methane over Ni supported on doped CeO$_2$: New insight on the role of dopants for CO$_2$ activation J. CO$_2$ Util. 2019, 30, 63-78.

Giuliano, A., Carpanese, M.P., Clematis, D., Boaro, M., Pappacena, A., Deganello, F., Liotta, L.F., Barbucci, A. Infiltration, overpotential and ageing effects on cathodes for solid oxide fuel cells: La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ versus Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ J. Electrochem. Soc, 2017, 164, F3114-F3122.


Boaro, M., Pappacena, A., Abate, C., Ferluga, M., Llorca, J., Trovarelli, A., Effect of redox treatments on Ce$_{0.50}$Zr$_{0.50}$O$_2$ based solid oxide fuel cell anodes J. Power Sources, 2014, 270, 79-91.

**INDUSTRIAL COOPERATION, PATENTS**

2019-2022 Treibacher AG (Austria) Development and characterization of perovskites for catalysis (responsible of laboratory activity). ~60K

2018-2019- INSTM convention with ENI for the characterization of catalysts for the direct oxidation of methane to methanol (responsible of laboratory activity). ~40K

2015-WO2015124595A1 “Method for the catalyzed reduction of halogen oxyanions in aqueous solutions” Renzo Rosei, Luca Conte, Alessandro Trovarelli, Marta Boaro, Stefano Gallucci, Massimo Centazzo, Rosanna Toniolo