



Chair:
Prof. Chiara Bertarelli

DOCTORAL PROGRAM IN MATERIALS ENGINEERING

The courses of the Doctoral Program provide Ph.D students in Materials Engineering with a common, basic knowledge on Materials Science and Technology, followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the skills required by technology in order to form qualified researchers who can manage the design, manufacturing and use of traditional and/or new materials.

Contents of the Doctoral Program

The Doctoral Course covers the following areas:

- *Polymers and composites*
- *Cements and ceramics*
- *Metals*
- *Biomaterials and materials for biomedical applications*
- *Processing and characterization of advanced metallic alloys*
- *Corrosion and durability of materials*
- *Innovative materials for civil and industrial engineering*
- *Materials Characterization (Microscopies, Scattering, Spectroscopy)*
- *Modelling and theoretical approaches to the study of materials structure and properties*
- *Micro and nanostructured materials*
- *Functional materials for applications in photonic, electronic and sensors*
- *Surface engineering and advanced coatings*
- *Materials for industrial design*
- *Meta-materials*
- *Transformation of materials*
- *Material for Cultural Heritage*

The courses face immediately advanced issues both in the main and elective courses. Different curricula are offered, which will be activated on the basis of the decisions of the faculty. The Doctoral program is characterised by high flexibility, in order to satisfy the needs of students that have to develop their research activity in different thematic areas. For this reason each student submit to the Faculty a “Curriculum” to be approved. The Courses offered deal with theoretical, experimental and modelling aspects. Several Courses comprise workshops and seminars, with the participation of invited internationally celebrated speakers. Students can use the most modern facilities for materials

synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The research activities related to the Ph.D. theses develop, full time, along the three years of the Ph.D. courses. Stages in industries or in national laboratories in Italy or abroad are offered. Each Ph.D. student are supervised by a professor of the faculty: the faculty evaluates the progress of his research activity and at the end of each year expresses a judgement on the continuation of the work for the subsequent year. At the end of the third year the Ph.D. student presents and defends, in a public hearing, his thesis work with a jury formed by three experts. The Ph.D. student is strongly encouraged to attend at national and international meetings and present papers in his specific field. The Ph.D. student is also assigned to give seminars on topical issues and/or to lecture on the specific fields of his research or on the cultural aspects related to his thesis.

The PhD Program in Materials Engineering requires the acquisition of 25 credits through attendance at Doctoral Courses (with positive evaluation in the examinations); in addition, attendance at National and International Schools are strongly encouraged.

- the remaining credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

Faculty:

The faculty is constituted by Professors from two Departments of Politecnico di Milano:

DIPARTIMENTO DI CHIMICA, MATERIALI E INGEGNERIA CHIMICA “GIULIO NATTA”		
Chiara Bertarelli (coordinator)	Francesco Briatico Vangosa (vice-coordinator)	Luca Magagnini
Fabio Bolzoni	Massimiliano Bestetti	Fabio Ganazzoli
Luigi De Nardo	Giovanni Dotelli	MariaPia Pedefferri
Marinella Levi	Valdo Meille	Stefano Turri
Guido Raos	Lucia Toniolo	Claudia Marano
Pasquale Vena	Elena Redaelli	
DIPARTIMENTO DI ENERGIA		
Marco Beghi	Andrea Li Bassi	Paolo Ossi

Professional skills achieved by PhD in Material Engineering:

The industrial world depends necessarily on a great variety of materials. Nowadays, it is easy to outline two industrial needs: i) development and innovation in the production, processing, application and conservation of traditional materials; ii) development of innovative materials for the production of new manufactured goods or devices to cope with the growing demands of modern technologies. Since these two kinds of industrial needs require specialized people a few specialized curricula are offered. On the other hand, the capabilities acquired through the courses, the research work and the teaching activity assure an adequate preparation to the academic career.

REFEREES (COMITATO DI RIFERIMENTO)

Edoardo Bemporad, Dip. di Ingegneria Meccanica e Industriale, Università Roma Tre	Marco Bernasconi, Dip. di Scienza dei Materiali, Università Milano Bicocca
Marco Ferrera, ST Microelectronics	Stefano Gialanella, Dip. di Ingegneria Industriale, Università di Trento
Alessandro Martucci, Dip. Ingegneria Meccanica, Università di Padova	Federica Bondioli, Dip. Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino
Stefano Radice, Solvay Specialty Polymers SpA	Riccardo Po', ENI SpA
Fiorella Pozzobon, ST Microelectronics	Stefano Carminati, ENI SpA
Francesco Stellacci, Dept. of Materials Science and Engineering, EPFL, Lausanne	

GRANTING AGENCIES

ST Microelectronics s.r.l.	RSE Ricerca Sistema Energetico
Fondazione Istituto Italiano di Tecnologia IIT	Istituto Nazionale di Astrofisica
SOLVAY SOLEXIS SpA	INSTM
eni SpA	Electrolux SpA
Faber SpA	InnovHub

PEDEFERRI'S DIAGRAM OF STAINLESS STEEL TYPE AISI 304L

Arash Azimi Dastgerdi - Supervisor: Prof. Fabio Bolzoni

Tutor: Prof. Maria Pia Pedferri

Pitting and crevice are localized corrosion forms of stainless steels, which occur in oxidizing chloride (or other halides) containing environments. These ions are quite common in natural environments (seawater, coastal zones, de-icing salts) or industrial ones (brines, process fluids). Chlorides are responsible of the local breakdown of the passive film (corrosion initiation); then, corrosion takes place by a macrocell mechanism in the presence of oxidizing environment, namely oxygen containing (corrosion propagation). Since the pitting and crevice corrosion rate is generally very high, between 1 and 10 mm/year, the initiation of these localized corrosion phenomena has to be prevented by proper material selection as a function of the aggressiveness of the environment. The localized corrosion initiation occurs when the corrosion potential is higher than passivity breakdown potential, which in turn depends on several factors related to the metal and the environment. In the thesis it is proposed to use the Pedferri's diagram in order to assess the localized corrosion behavior of stainless steel (namely type AISI 304L steel, very used in industrial applications) in the presence of chlorides. The diagram, originally proposed by prof. Pietro Pedferri in the '90s for carbon steel in chloride contaminated concrete, defines corrosion, perfect and

imperfect passivity zones (according to Pourbaix), as a function of the potential and chloride content (Fig. 1).

Since the measurement of the passivity breakdown potential (E_{bd}) and re-passivation potentials (E_{rep}), necessary for the definition of the diagram, is known to be affected by the experimental method, it is essential to find the most reliable electrochemical method. Moreover, even for a single material, the generation of the diagram requires huge number of experimental tests, combining different values of the environmental factors. In this thesis, after an extensive bibliographic research, a test protocol is defined considering different electrochemical tests, i.e.

potentiodynamic and potentiostatic polarization tests. In the first, chloride content is fixed and the potential is changed continuously with a fixed scan rate, while in the second the potential is kept constant and the chloride content is increased until the initiation of localized corrosion. Despite the scattering of the results, intrinsic for localized corrosion, the agreement between breakdown potentials obtained by potentiodynamic polarization and critical chloride concentrations obtained by potentiostatic polarization was good, and potentiodynamic polarization was selected for the following tests (Fig. 2).

In the second part of the thesis, the effect of pH, temperature and

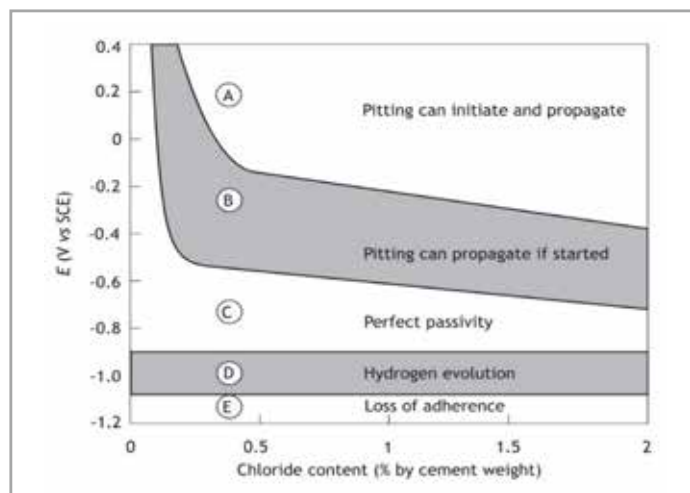


Fig. 1 - Pedferri's diagram of carbon steel in concrete.

chlorides content on the localized corrosion of AISI 304L stainless steel has been investigated by design of experiment (DOE) method. This approach optimizes the selection of the experimental conditions, reducing the number of tests, as well as developing a mathematical model through a polynomial regression equation.

The regression equation was developed from E_{bd} extracted from potentiodynamic polarization and showed the contribution of the variables on the pitting corrosion initiation. After the analysis of the regression equation a simplified equation, that linearly correlates the E_{bd} with temperature, pH and chloride content (log) has also been proposed. The slope of the line depends on the pH while the intercept depends on pH and temperature as it is shown in the

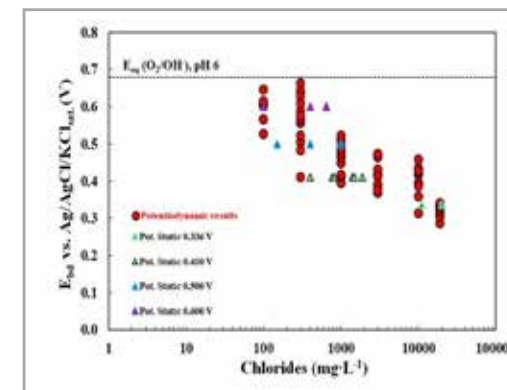


Fig.2 - Comparison of potentiodynamic and potentiostatic polarization tests (AISI 304L stainless steel, room temperature, pH= 6).

following Equation.

$$E_{bd}(V \text{ vs. Ag/AgCl/KCl}_{sat.}) = A - B \cdot \log(Cl_{mg \cdot L^{-1}}^{-1})$$

$$A = -0.0078 \cdot T(^{\circ}C) + 0.083 \cdot pH + 0.17$$

$$B = 0.015 \cdot pH - 0.0078$$

The absolute value of the slopes in the chloride concentration range of 100–10000 $mg \cdot L^{-1}$ and pH near to neutrality are in very good agreement with the literature. The results obtained in this research have been compared with the susceptibility to pitting and crevice corrosion of AISI 304L in some practical conditions, with a fair agreement in most cases. The Pedferri's diagram of AISI 304L stainless steel for various chloride containing environments, pH, and temperature is determined. Figure 3 shows an example of this diagram, for pH= 6 and temperature 20 °C. The solid line is generated by the aforementioned Equation

(1) and points are the experimental ones. Since localized corrosion is characterized by and intrinsic variability, dotted lines has been introduced representing the range of E_{bd} found in the experimental tests. The repassivation potential results are also reported in Fig. 3.

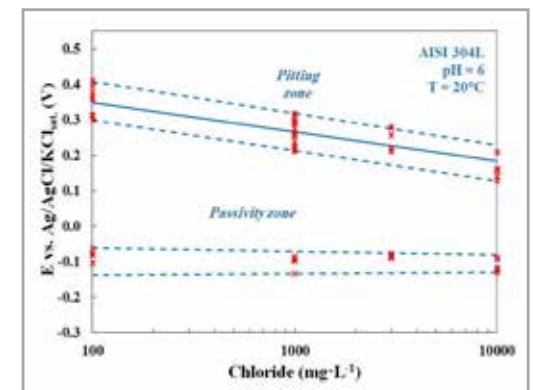


Fig.3 - Simulation of Pedferri's Diagram of AISI 304L stainless steel at pH 6 and T=20 °C.

IN-SILICO AND IN-VITRO STUDIES FOR THE DESIGN AND ASSESSMENT OF NI-TI BIOMEDICAL DEVICES

Francesca Berti - Supervisors: Prof. Francesco Migliavacca, Prof. Lorenza Petrini

Tutor: Prof. Pasquale Vena

Nickel-Titanium (Ni-Ti) is a shape memory alloy widely used in many engineering fields due to its temperature-dependent and pseudo-elastic properties. Its mechanical response exhibits a strong nonlinearity, which requires particular attention during the material static and fatigue characterization. Many efforts have been spent in the last decades on Ni-Ti alloys, but many deficiencies are still present due to their multi-factorial mechanical and modellistic issues.

The objective of this thesis is to increase the awareness of this particular material, focusing on its employment in the design and assessment of biomedical devices. In Chapter 1, an introduction to the state of the art of Ni-Ti material properties is provided, with attention on those particular aspects treated in the following.

The first part of the thesis is specifically focused on material properties and constitutive modeling. Recently, a new constitutive model was formulated that accounting for inelastic strains due to not-completed reverse phase transformation (not all the stress-induced martensite turns back to austenite) or/and plasticity and their accumulation during cyclic loads. Chapter 2 collects the model formulation and the results of some validation tests (uni- and multi-axial). Complex geometry and micrometric dimensions characterize stents:

their minimal feature (v-struts) is around 200 μ m width. Moreover, the characteristic non-linearity derives from a phase transition, which does not happen uniformly, but more as a propagation. In order to map displacements or strain with sufficient accuracy, it would be desirable to be able to perform measurements directly on the specimen. Digital Image Correlation (DIC) seems an appropriate method, although the current practice of painting speckles onto the sample surface appears too coarse, the finest painted speckle

being roughly the same size of the stent v-struts size. Chapter 3 contains the efforts of conceiving a finer scale DIC-technique, based on the optical properties of low-coherence speckles (lcs). Ni-Ti behavior under cyclic loads has been widely investigated in the literature: information obtained from fatigue testing is a key element in the establishment of design criteria to protect against component failure. In this frame, even if no specific standard treats this subject, Chapter 4 summarizes the results of uniaxial tensile, bending and torsional fatigue

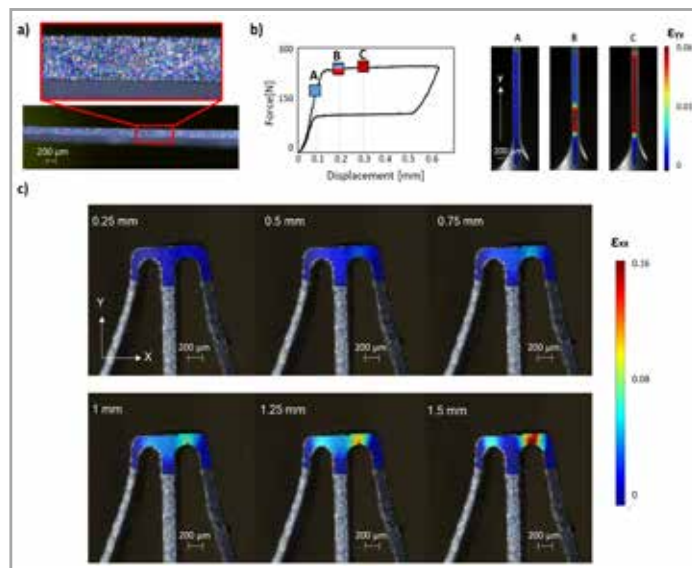


Fig.1 - a) lcs-DIC technique allows obtaining polychromatic speckles on micrometric Ni-Ti wire specimens; b) characteristic force-displacement curve obtained during a tensile test on the wire specimens and corresponding strain values along a portion of the specimen gauge length at different loading increments, with their corresponding colour maps; c) lcsDIC allowed the strain field measurement on the stent v-strut during its loading with a spatial resolution of few microns

tests on specific material specimens. Computational tools may be of great help when coupled with experiments in modeling Ni-Ti non-linearity, but great carefulness should be paid in order not to make mistakes in the interpretation of the results, especially in the case of bending-dominated problems involving diamond-shaped specimens.

In the second part of the thesis, two different biomedical applications of Ni-Ti alloys are discussed. In particular, it was chosen to treat peripheral stents as for pseudo-elasticity (Chapter 5), whereas an innovative self-knotting suture was

investigated as for the shape-memory effect (Chapter 6).

Ni-Ti peripheral stents fatigue assessment is an up-to-date topic and still a multi-factorial open issue for both the complexities of the geometry and the material characteristic curve. The difficulties increase when the particular material is coupled with a complex device geometry, such as a stent, subjected to multi-axial loads. A deep investigation of the role of the stent design and non-linear material was provided to demonstrate the existence of local non-proportionality even under proportional boundary conditions. Then, the results of an

experimental fatigue campaign were used to validate a set of FE models and to identify the best fatigue criterion, among already existing ones, for describing Ni-Ti behavior. This can be a useful tool in both academic research and industry for a better understanding of the device performances and a more reliable design and manufacturing. Shape memory effect has been always used in the biomedical field even if the majority of implantable devices exploits pseudo-elasticity. A recent SME application was identified in the deep field surgery when the intrinsic difficulties led to the development of an innovative suture wire able to self-knotting itself. To better address the functional and structural requirements, a finite element model of the device was prepared and validated through an extensive experimental campaign. Then, it was used to test the device under many and different loading conditions to catch any strength and limitation toward the use in the clinical practice.

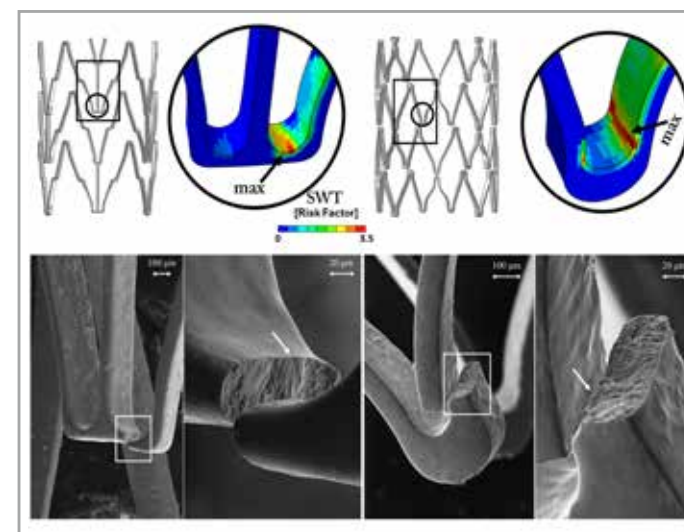


Fig.2 - Results of the coupled in-silico in-vitro study for the fatigue assessment of peripheral stents according to the Smith-Watson-Topper criterion. The FE analysis allowed the identification of the most critical area for fatigue failure, which resulted in the location of the experimental fracture.

PREPARATION AND CHARACTERIZATION OF INNOVATIVE CATHODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

Giulio Cordaro - Supervisor: Cinzia Cristiani

Tutor: Giovanni Dotelli

Throughout the centuries, energy production has been a fundamental aspect of any social, economic and technological progress. Recently, the energy market is demanding a revolution towards sustainable solutions. The use of hydrogen as energy vector is considered the future of energy production, conversion and storage. Among the technologies of the future hydrogen economy investigated in last years, Solid Oxide Fuel Cell (SOFC) is considered very promising due to the extremely high operating efficiency, high fuel flexibility and tolerance towards pollutants. The reduction of the operating temperature from 800-1000 °C to an intermediate range (500-700 °C) is the main challenge of the research to improve the lifetime and the applicability range of this technology. The main drawback of IT-SOFC is the dramatic drop in electrocatalytic activity of single components, especially the oxygen reduction reaction, controlled by the cathode. Innumerable efforts have been invested in the investigation of cathode materials with high efficiency, compatible with electrolyte materials and long-term stability in operating conditions.

This PhD thesis is focused on the production and characterization of innovative solid oxide compounds suitable for application as cathode for IT-SOFCs. Different families of solid oxides with a layered perovskite structure are investigated.

Analytical techniques, such as X-Ray Powder Diffraction (XRPD), Differential Thermal Analysis-Thermogravimetry (DTA-TG), Temperature-Programmed Reduction (TPR), Scanning Electron Microscopy (SEM), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and titrations, are applied for the chemical, structural and morphological characterization of the samples. The electrochemical characterization is investigated through Electrochemical Impedance Spectroscopy (EIS) measurements, performed on symmetrical electrolyte-supported cells, and conductivity tests, on sintered bar. Several techniques are carried out to elaborate the experimental data, e.g. Rietveld refinement of diffraction spectra, Distribution of Relaxation Times (DRT) and Equivalent Circuit Model (ECM) analysis on impedance results. The first class of compounds evaluated

as IT-SOFC cathode is the double perovskite structure. Particular attention is focused on cobalt-based perovskites, due to promising performance and compositional versatility. The investigation of Ba deficiency in Nd-based layered cobaltite is carried out within the NBC series of materials ($\text{NdBa}_{1-x}\text{Co}_2\text{O}_{5.6}$). The best electrochemical performances are obtained for the sample with a 10% Ba deficiency ($\approx 450 \text{ S/cm}$ and $0.10 \Omega\cdot\text{cm}^2$ at 700°C) that achieved a tenfold improvement compared to stoichiometric compound. The main processes that contribute to the global resistance are surface electronation and ion transfer across the electrolyte/electrode interface. The effect of Fe doping on cobalt sites of the NBC composition is investigated together with Ba deficiency in the $\text{NdBa}_{1-x}\text{Co}_{2-y}\text{Fe}_y\text{O}_{5.6}$ (NBCFd) series of double perovskites. An ordered layered

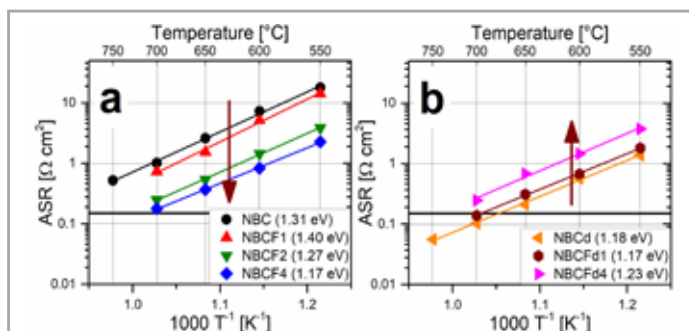


Fig. 1 - Arrhenius plots of the Area Specific Resistance (ASR) for the stoichiometric (Panel a) and deficient compounds (Panel b) of the NBCFd series of double perovskites.

structure with tetragonal lattice ($P4/mmm$) is found, whose cell volume increases with Fe doping and decreases with Ba deficiency. A high total conductivity ($150\text{--}450 \text{ S/cm}$ at 700°C) is measured despite the hindering effect of Fe. In stoichiometric compounds, Fe doping reduces the polarization resistance (Fig. 1a), while an increase is observed in Ba-deficient samples (Fig. 1b). ECM and DRT results reveal that the rate determining step is the surface electronation, but also ion transfer at the electrolyte interface significantly contributes to the Oxygen Reduction Reaction (ORR) global resistance.

The characterization of a compound with the Ruddlesden-Popper layered structure is carried out with different synthesis procedures to evaluate the

effect on electrochemical activity. The novel composition $\text{La}_{0.8}\text{Sr}_{1.2}\text{Fe}_{0.9}\text{Cu}_{0.1}\text{O}_4$ (LSFC) is characterized as IT-SOFC cathode. Wet synthesis techniques show an improvement of the microstructure, which however, does not enhance the electrochemical performances. This indicates that the ORR mechanisms involve the Triple Phase Boundary (TPB), which suggests the applicability as composite cathode material. The last group of investigated materials is a series of solid oxide cuprates with complex perovskite structure and chemical formula $\text{PrBa}_2\text{Sr}_x\text{Cu}_3\text{O}_{6+x}$ with $x = 0$ (P) and 0.5 (PS). The electrochemical analysis shows promising results for both the samples, without significant changes related to Sr doping (PS+PrDC: $0.17 \Omega\cdot\text{cm}^2$ at 600°C, Fig. 2).

The Pr123 structure presents very high sensitivity to temperature variations, because the material is composed by a mixture of tetragonal (Pr123-T) and orthorhombic (Pr123-O) structures. This phase transition is investigated with a series of materials produced using calcination ramps with different cooling rates. The O/T ratio influences both the oxygen content, the conductivity and the EIS results. The more Pr123-T phase is oxidized into Pr123-O, the higher conductivity values are measured. An improvement related to slower cooling ramps is observed also for Area Specific Resistance (ASR) results at low temperature, but above 600°C the curves present significantly different slopes (Fig. 3). This indicates a complex mechanism involved in the ORR for this peculiar structure.

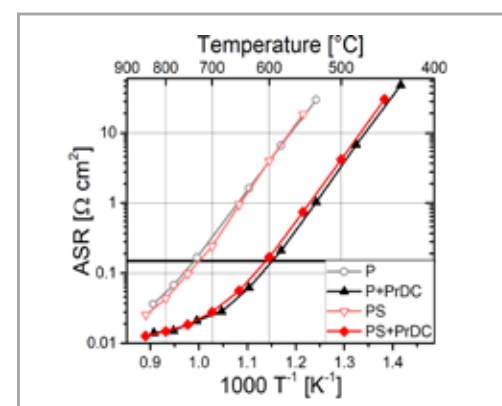


Fig. 2 - Arrhenius plots of the Area Specific Resistance (ASR) for the P and PS samples with and without the $\text{Ce}_{0.7}\text{Pr}_{0.302-\delta}$ (PrDC) interlayer.

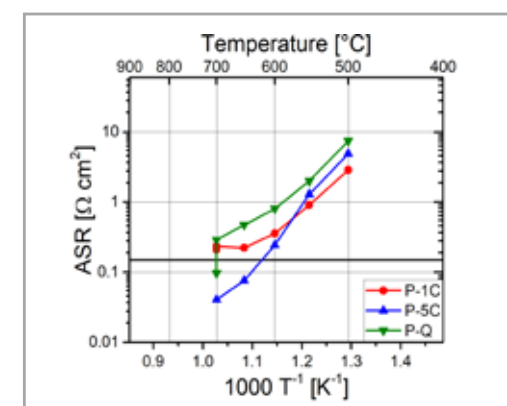


Fig. 3 - Arrhenius plots of the Area Specific Resistance (ASR) for the P composition with $\text{Ce}_{0.7}\text{Pr}_{0.302-\delta}$ (PrDC) interlayer produced with different calcination cooling rates: $-1 \text{ }^\circ\text{C min}^{-1}$ (P-1C), $-5 \text{ }^\circ\text{C min}^{-1}$ (P-5C) and quenched sample (P-Q)

MATERIAL-BASED *IN VITRO* MODELS OF THE RESPIRATORY TRACT

Daniela Patrícia Peneda Pacheco - Supervisor: Prof. Paola Petrini

Tutor: Prof. Luigi De Nardo

Cilia, mucus and the periciliary layer are essential units of the mucociliary clearance of human airways. Inhaled noxious agents, drugs and bacteria are entrapped within mucus - a three-dimensional polymeric hydrogel.

Mucus is continuously propelled by the action of ciliary beating towards the pharynx, where it can be expectorated or swallowed, avoiding any risk of infection or bacteria stagnation. This is only possible due to a watery intermediate blanket - the periciliary layer (PCL) -, which properties enable cilia to beat and propel mucus. The harmonised interaction between mucus, PCL and cilia guarantees the elimination of inhaled noxious agents and bacteria, but also limits the time of retention of a drug, which might be eliminated before reaching the epithelium.

Diseases like cystic fibrosis (CF) are characterised by abnormal mucus, PCL depletion and minor ciliary motion, which results in mucus accumulation. Mucus accumulation favours the establishment of chronic bacterial infections that ultimately lead to lung malfunction and patient death. In this way, models of both physiological and pathological airway apparatus would highly benefit drug development to find new pharmacological treatments for diseases affecting the airway apparatus.

To model the airway apparatus, its

complexity was disassembled to develop different material-based *in vitro* models of both mucus and cilia. These models address the different barriers of drug diffusion imposed by mucus and cilia: interactive, steric and dynamic barriers. To produce mucus models, different materials were selected based on their presence, abundance and structural-property relationship in the human mucus in physiological and pathological states. Mucin was selected as the major component of all developed mucus models, which exhibit variable viscoelastic properties and chemical composition. The versatility of the fabrication method and chemical composition enables to easily include key chemical entities of mucus.

Mucin was able to interact with drugs with previous reported interaction, and drug diffusion was dependent of the size of drug or particles unravelling the impact of the mesh size of mucus models. The flexible chemical composition of these models is expected to distinguish which component(s) interact with drugs at early stage of drug development. Thus, enabling the development of new strategies to modulate drug diffusion to either promote interaction (mucus adhesive particles) or diffusion (mucus penetrating particles) with/through mucus. The steric barrier of these models resultant from chemical interaction

may instead aid the development of pharmacological therapies that may disrupt such interactions to reverse the effects of mucus accumulation so relevant in chronic obstructive pulmonary diseases, such as cystic fibrosis and chronic obstructive pulmonary disease. The potential to exploit the mucus models as a platform to determine antimicrobial susceptibility *in vitro* was proven by inducing infections of *Pseudomonas aeruginosa*, the most prevalent bacteria colonising cystic fibrosis

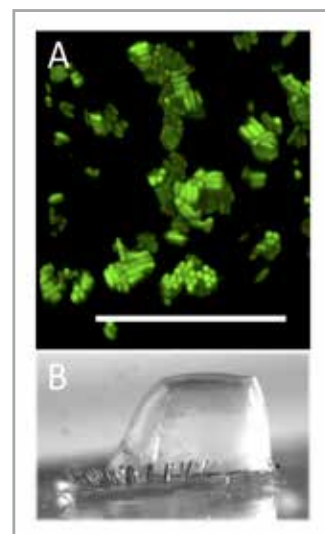


Fig. 1 - A) Infected mucus models depicting bacterial aggregates that resemble those of human infected mucus; and B) material-based model of human mucociliary transport composed of mucus model, PCL-simulant and magnetic artificial cilia.

mucus. *Pseudomonas aeruginosa* was able to colonise and form bacterial aggregates previously observed on infected cystic fibrosis sputum (Fig. 1A). Mucus models infected with *P. aeruginosa* were treated with three different antibiotics to which *P. aeruginosa* is sensitive and compared in effectiveness to standard bacteria cultures. The sensibility difference between the mucus models and planktonic cultures confirmed the well-reported mismatch between planktonic conditions and clinical outcomes. These results indicate that the mucus models are a promising substrate to recreate lung microbiota for antimicrobial screening. The mucus models are compatible with state-of-art diffusion models (e.g. parallel artificial membrane permeability assay - PAMPA - membranes), Transwell® systems and dynamic systems. The reported results indicate that mucus models may provide a tool to screen a wide range of molecules commonly administered to cystic fibrosis patients, including antimicrobial agents, mucolytics, anti-inflammatory drugs, CFTR-modulators, bronchodilators. In principle, these models are compatible with cell studies, which may provide a more representative tool for risk assessment of human exposure to nanoparticles, pollutants, tobacco, electronic cigarettes, among others. To take into consideration the combined effect of steric, interactive

and dynamic barriers, magnetic artificial cilia were optimised and coupled with mucus models. The magnetic artificial cilia worked as micro-pumping hair-like systems that were able to beat once actuated by an external magnetic field. To model physiological mucociliary transport, an intermediate periciliary-layer simulant was introduced to guarantee mucus propulsion by the action of artificial cilia, as described in human physiological mucociliary clearance apparatus. This allowed the evaluation of mucus transport by simultaneously monitoring mucus rheology and ciliary dynamics (Fig. 1B). The Lego®-like character of this system allowed to easily alter the composition of each unit individually to then assess its impact on the overall response. Indeed, by simply varying the chemical composition of the mucus models or the magnetic field employed to control cilia motion, it was possible to model both physiologic and pathological scenarios. The composition of the simulant of the periciliary layer can also be changed to closer achieve physiological mucus speed. The model of mucociliary clearance addressed the simultaneous presence of mucus, PCL and cilia and it can be exploited to evaluate the impact of external agents over mucociliary transport, as particles, nicotine, pollution and bacteria. This model may be modified to mimic the route of

the ovum from ovary to uterus by the action of beating cilia in the Fallopian tubes, to investigate strategies that tackle infertility.

All conceived models strictly rely on materials, thus offering higher reproducibility across different laboratories, while not requiring animals or cells, as well as specific equipment and characterization techniques for their evaluation. Indeed, a set of experimental methods, mathematical modelling and imaging analyses were established to provide a deep characterization during the development of material-based *in vitro* models. All proposed approaches may be used to broaden the understanding of drug permeability across mucus, as well as mucus transport along human airways. These models might constitute a valid new tool to deeply investigate pathophysiological human mechanisms and/or for screening new therapeutic treatments, even attempting patient-specific strategies.

INVESTIGATION OF THE PROPERTIES OF NOVEL NANOCOMPOSITES FOR THE PROTECTION OF STONE MATERIALS

Marco Roveri - Supervisor: Prof. Lucia Toniolo

Tutor: Prof. Chiara Bertarelli

The maintenance of historical architecture represents one of the topical aspects within the more general issue of preserving our cultural heritage. When exposed to the environment, stone monuments are subjected to a host of decay phenomena, which determine an irreversible and, in the long run, inevitable degradation of their cultural value. The application of protective treatments is generally aimed at preventing the onset of decay phenomena on sound stonework or to limit the progress of deterioration on monuments that have been exposed for long time. Among the deteriorating factors at work, the penetration of water into the stone porous structure holds the first place, yet in a polluted environment such as most present-day urban areas, natural agents of decay combine with anthropogenic ones. Thus, strategies for stone protection have become increasingly concerned with adopting a multi-functional approach, that is, coping with water penetration on one side and the soiling and corrosion from airborne pollutants and microorganisms on the other. In this regard, nanotechnology has come to play a significant role over the last ten years. The development of hybrid nanocomposites, i.e., products relying on the combination of inorganic nanoparticles (NPs) with polymeric matrices, has given rise to a new generation of conservation

treatments, which combine the hydrophobizing properties of certain polymeric materials to the photocatalytic and/or antimicrobial properties of inorganic nanomaterials such as titania and zinc oxide NPs. The efficacy of these treatments varies strongly from stone to stone, generally resulting from a complex interaction. As a rule, only direct testing can help identify the most effective treatment for each stone. Nevertheless, scientific research is likely to give a valuable contribution in this regard, in that it can help rationalise the correlation between the properties of stones and treatments and the final protective performance. This thesis pursued a systematic investigation of the properties and performances of a set of nanocomposite formulations that were developed within the H2020 Nano-Cathedral project. The aim of this project was to bring the newest results of current scientific research on nanomaterials for the purpose of stone conservation to the level of a ready-to-use tool for conservation practice. The specific objective of the thesis was to gain insight into the relationship between the characteristics of stones, the properties of the treatments and their performance. Six stones with widely different characteristics (pore-size distribution, mineralogical composition, texture) were chosen

as substrates for the investigation of sixteen nanocomposite formulations. After a preliminary testing of these formulations, six products with photocatalytic or antifouling functionalities were selected and their performances were studied through a comprehensive set of laboratory tests. Specifically, water absorption by capillarity, water vapour permeability, static contact angle and photocatalytic/antifouling activity were evaluated, alongside SEM and AFM observations of treated stone surface morphology. Two of the six selected nanocomposites, which consist of silane matrices with the addition of titania NPs, were investigated in greater depth. The behaviour of these photocatalytic products was discussed at the light of the different stone properties, focusing on the effects of product penetration and the modification of the stone surface morphology (Fig. 1). As a very general observation, products with lower penetration ability (higher viscosity, reactivity and particle size) perform better on stones with a higher fraction of large pores, whilst products with higher penetration work best on stones where small pores are predominant; furthermore, although a good penetration is necessary to achieve a good protection, the former should not be too much in order to keep the pores permeable to water vapour.

While not modifying the protective behaviour of the silane matrices with respect to properties such as water repellency and water absorption reduction, titania NPs impart mild photocatalytic properties, which help oxidise organic and inorganic pollutants deposited on the surface. As a side effect, the same NPs cause the oxidation of the silane matrices and the loss of some of the protective efficacy upon prolonged exposure to sunlight. However, since this effect does not extend to the inner pore structure, treatments retain most of their ability to reduce the capillary absorption of water.

The relationship between the chemical modification of the water-stone interface and the protective performance was a further topic of investigation. Assessing this modification is a rather difficult task, for the said interface includes part of the pores that are not easily inspected through microscopy observation. In this study, an electrokinetic technique based on streaming potential measurements was used to evaluate the surface modification, allowing to compare the different treatments. Finally, a mechanistic model of the stone-treatment interaction and, specifically, of pore hydrophobization, was conceived. The fundamental assumption of this model, which is partly based on experimental evidence, is that larger pores are hydrophobized to a greater extent as

compared to smaller pores, because they allow the treatments to more easily penetrate and settle on their inner surface (Fig. 2). Combined with a semi-empirical model of the capillary imbibition dynamics, this assumption was used to describe the effect of the treatments in terms of water absorption reduction.

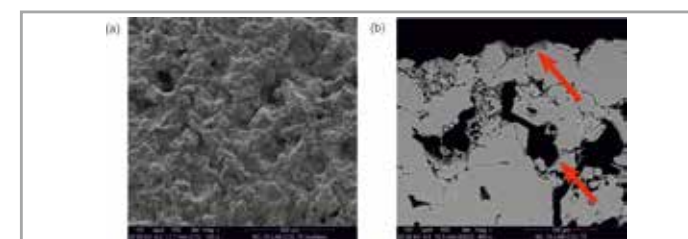


Fig. 1 - SEM images of (a) surface and (b) cross section of Obernkirchen sandstone specimen treated with one of the products.

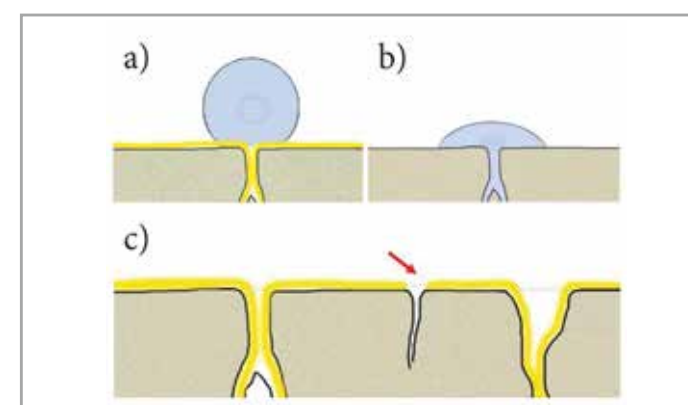


Fig. 2 - Assumptions for the modelling of pore hydrophobization: (a-b) hydrophobized pores reduce the water absorption rate to an extent depending on the penetration of the treatments; (c) a greater number of large pores are hydrophobized compared to smaller pores (see arrow).