

Development and Characterization of Oxygen Carriers for Chemical Looping Combustion

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The main difficulty with carbon capture is high energy penalty and costs for gas separation processes, common for pre-combustion capture, post-combustion capture and oxyfuel combustion. Chemical Looping Combustion (CLC) is a relatively new combustion technology that can be applied as a power production technique with inherent separation. As such Chemical Looping Combustion can be considered a promising CCS technology for the capture of the greenhouse gas CO₂. The CLC process mostly is configured as two coupled fluidized bed boilers (CFB), but also a configuration with packed bed reactors can be considered. In order to transfer oxygen from the combustion air to the fuel, oxygen carriers are used. This avoids direct contact between air and fuel. After condensation of water, relatively pure CO₂ is obtained in a separate exhaust stream from the fuel reactor, making energy consuming flue gas separation unnecessary. Chemical looping technology is investigated for a variety of fuels: natural gas, but also liquid and solid fuels like coal and biomass, the latter resulting in a negative CO₂ footprint.

Chemical looping technology is gradually maturing, with both the number as well as the size of research and demonstration plants growing from kW to MW, with 100-1000 MW on the drawing board. In the heart of CL technology is the oxygen carrier, which is indispensable for transferring the oxygen to the fuel. Over the past years a wide variety of materials have been proposed for this role, ranging from bulk mineral powders to oxygen carrier particles engineered for shape, size and composition. Several routes for the fabrication of oxygen carriers are being investigated: from simple size reduction and classification of bulk minerals to more elaborate processes comprising industrial process steps like spray drying or incipient wetness impregnation.

A major part of the research effort is being devoted to development oxygen carriers. For fluidized bed application, the spray drying technique appears to be very well suited. Spray dried oxygen carrier particles for fluidized bed application are characterized by high sphericity and good fluidization properties. Further, the microstructure should on the one hand assure for thermo-chemo-mechanical integrity and high attrition resistance, as well as good interaction with gaseous compounds on the other hand. Promising materials are Ni-, Cu-, Fe- or Mn-based, each with their pros and cons. Some of these materials release oxygen at the typical combustion temperatures. This so-called oxygen uncoupling is highly desirable since it contributes to full conversion of fuels.

Electrical Discharge Machinable Ceramic Composites

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Due to their extreme hardness ceramic composites are ideally suited for application in wear intensive parts and machinery. However, this also makes them notoriously difficult to machine using classical cBN and diamond grinding tools. Electrical Discharge Machining (EDM) allows for the fabrication of intricate parts out of ultrahard electrically conductive ceramics. In this presentation several relationships between microstructure, surface quality and EDM behaviour will be elaborated by virtue of two novel ceramic materials, namely B₄C-TiB₂ and Si₃N₄-Carbon nanotube composites. Parameters such as grain size, phase dispersion and phase composition are linked to Material Removal Mechanisms (MRM's), Material Removal Rates (MRR) and surface quality. It is shown that the starting powders, processing route and PECS parameters have a strong influence on the EDM behaviour, proving that that the EDM behaviour can already be considerably influenced and engineered during the ceramic composite processing stage.

Completely Recyclable Concrete for a More Environment-Friendly Construction

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Although concrete is a durable material, it has a big impact on the environment due to its high production volumes. This impact is mostly related to the consumption of virgin raw materials, the production of waste and the emission of carbon dioxide. For these reasons, many studies in the field of concrete research focus on the recycling of solid wastes in concrete, lowering the need for virgin raw materials and avoiding waste to be landfilled. However, most of these recycling opportunities often arise from the search for new synergies between usually unrelated partners. Also, recycled products still suffer from a low acceptability caused by a lack of trust in the quality of these products and in some cases by the higher cost of recycled materials compared to natural raw materials. From here and inspired by the cradle-to-cradle concept, the idea emerged to design concrete as raw material for cement production. The necessary condition for the production of such CRC is that its chemical composition is equivalent to the one of a cement raw meal.

Within this study several CRC compositions were designed. Within the design methodology, the chemical composition of CRC is evaluated by the potential mineralogy using the Bogue formulas and the compositional parameters as used in the industry (LSF, SM, AM and HM). It was found that the Bogue formulas are sensitive for small changes in chemical composition. For this reason the compositional parameters were found decisive in the design process.

Although the CRC concept is intended to be sustainable, of course it should also have a good performance regarding workability, strength and durability. The strength and durability of CRC are mainly affected by the use of fly ash. Three durability aspects of CRC were studied, namely the resistance against carbonation, chloride ingress and freeze-thaw attack with de-icing agents. Furthermore the study focussed on the possible application of copper slag on the one hand and the deceleration of the fast setting that resulted from the combination of calcium aluminate cement and blast furnace cement on the other hand.

The clinker and cement regenerated from CRC should also be of sufficient quality. The quality and hydration of the regenerated cement was studied using light microscopy, thermal analysis and XRD Rietveld analysis. In addition to the experimental program, the hydration of the regenerated cement was also investigated by thermodynamic modelling. Both the clinkering reactions and the hydration process were found comparable for regenerated and ordinary Portland cement.

In the end the question remains whether the CRC concept is sustainable. For this purpose a life cycle assessment was conducted. From these results it was concluded that the environmental impact of concrete is dominated by the cement manufacturing process, the required transportation and the use of fly ash. Due to its low clinker content, the impact of the cement manufacturing process will be lower for CRC. However, the longer transport distances expected for the recycling of CRC and the impact of the use of fly ash will increase the impact of CRC compared to traditional concrete. Considering the overall impact on the environment it was found that only a CRC with a low clinker content and high strength can compensate for the extra costs related to transportation. However, due to the available CO₂ free lime, the emission of CO₂ can be reduced significantly.

Looking at the whole picture, some logistic and practical problems will need to be tackled for the CRC concept to succeed. A well-considered tracking system and selective demolition will be required. Additionally the dependence of the raw material requirements on the used fuels in the clinkering process results in the non-existence of one ideal raw meal composition. In comparison with today's recycling opportunities for concrete, the CRC concept is thus more complex. The opportunities of the CRC concept however lay within the possibility of safely disposing (some) toxic wastes and the possibility to recycle deteriorated concrete if proper dilution is applied.

Selective Laser Sintering and Melting as additive manufacturing methods to produce alumina parts

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Additive manufacturing (AM; aka 3D printing) has the potential to rapidly shape parts with an almost unlimited shape freedom. Variants of the following powder metallurgy (PM) route, with an additive manufacturing shaping step, were explored to produce ceramic parts: (i) powder synthesis, (ii) additive manufacturing, (iii) binder removal, (iv) furnace sintering and alternative densification steps. In this study, alumina (Al_2O_3) parts were produced since Al_2O_3 is currently the most commonly used ceramic material for technical applications. Further, two AM methods were investigated as possible shaping steps for the production of alumina parts: indirect Selective Laser Sintering (indirect SLS) and direct Selective Laser Sintering/Melting (direct SLS/SLM).

To explore indirect SLS, different powders, with an agglomerate size of about 10-100 μm and consisting of a 0.3 μm alumina particles and a polymer binder phase (i.e. composite alumina-binder agglomerates), were irradiated by a laser beam. Five different alumina-binder agglomerates were investigated: alumina-polyamide agglomerates produced by ball milling, alumina-polystyrene powder produced by dispersion polymerization and alumina-polyamide, alumina-polypropylene and alumina-carnauba wax-low density polyethylene powders produced by temperature induced phase separation (TIPS). During subsequent SLS, the laser irradiation, which melts only the binder phase, selectively consolidates the powder agglomerates layer by layer. After subsequent binder removal and furnace sintering, alumina parts, containing inter-agglomerate pores, were obtained. In order to reduce the inter-agglomerate voids, the possibility to include the following steps into the PM process chain was explored: (i) irradiating the powder layers multiple times instead of only once (i.e. laser re-melting), (ii) cold, quasi and warm isostatic pressing the SLSed parts and (iii) infiltrating the parts obtained at different stages of the PM process. As a result, freeform shaped alumina parts with densities up to approximately 90% could be obtained. In order to produce higher quality ceramic parts through indirect SLS, the inter-agglomerate pores should be avoided or eliminated.

To explore direct SLS/SLM of alumina parts, an experimental setup was developed and tested. The experimental setup enabled to selectively irradiate densely packed layers of alumina powder, with a particle size of about 0.3 μm and without binder phase, at uniform temperatures up to 800°C. After a subsequent furnace sintering step, alumina samples with a grain size smaller than 5 μm could be obtained. Since small grain sizes are needed for the production of ceramics with good mechanical properties, this proves the possibility to fabricate high quality monolithic ceramics through direct SLS/SLM.

The surface chemistry of metal oxide nanocrystals; theory and applications

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Ceramic nanocrystals (NCs) are of general interest because of their possible applications in catalysis, gas sensing, LED's, nanocomposites, etc. However after synthesis, the formed NCs need to be properly processed in order for them to be used in applications. Hence the preliminary importance to gain knowledge over the surface chemistry of the NCs. In this contribution, we focused on hafnium oxide as a model system and subsequently validated the theory with other oxides.

HfO₂ NCs are solvothermally synthesized in benzyl alcohol with microwave heating. The surface of the thus obtained charge stabilized NCs can be subsequently modified with fatty acids and oleylamine to allow solubility in nonpolar solvents. Concomitantly, clusters are broken up, yielding the constituting individual particles. We present here a detailed study of the fundamental (acid/base) processes during the surface modification.

We also demonstrate that there is a crucial difference in surface chemistry between these metal oxide NCs and the more widely studied metal sulfide and selenide nanocrystals, such as PbS and CdSe. The electronegative property of oxygen allows for protons to be accommodated at the surface of HfO₂ NCs and one can see the binding event of a carboxylic acid on a metal oxide NC as a dissociative process. This is in contrast to the case of other chalcogenide NCs where only the carboxylate binds to the surface metal ions and the proton is removed during the binding event.

Subsequently, we show the practical implications of our fundamental findings. Ligand exchange reactions which before were considered impossible do take place at the metal oxide NC surface, e.g., exchange of X-type ligands for L-type ligands. Even more, due to the surface protons, acid catalyzed organic reactions could proceed in the presence of the HfO₂ NCs. This catalytic process was properly investigated for the esterification of ethanol with oleic acid.

In a second application, all inorganic nanocomposites were synthesized. HfO₂ NCs were distributed in a matrix of a High Temperature Superconductor, YBa₂Cu₃O_{7-x}. In order to do so, the NC surface was modified via ligand exchange to transfer the particles from apolar to polar solutions while maintaining impeccable colloidal stability. The transfer is necessary since the YBa₂Cu₃O_{7-x} precursor solution is methanol based. The resulting ink (NCs + precursor solution) was deposited via spin coating and after epitaxial film growth the superconducting nanocomposite was retrieved and its superconducting properties were evaluated.

In conclusion, metal oxide NCs hold protons on the surface, in contrast to metal selenides or sulfides. This characteristic allowed for unexpected catalytic activities

Tungsten carbide based composites for circuit breaker applications

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WC-Ag and W-Ag refractory electrical contacts belong to one of the most important contact material families used in state-of-the-art circuit breakers which operate at a wide range of currents (10-630-6300 A) in air depending on their application. During a short circuit or overload (5-250 kA), the contact must "open" to protect the remaining circuit. Consequently, an arc is generated which is fuelled by the plasma generated from ionization of molecules in air which reaches temperatures close to 20000°C. The superior thermal and electrical conductivity of silver combined with adequate mechanical and arc erosion resistance of a refractory carbide, makes it the ideal material for usage under severe arcing conditions. The hard WC particles suspended in the soft Ag matrix inhibits the contacts to weld together at such high temperatures.

In the present study, spark plasma sintering is explored as a new densification route and compared with the conventional densification process by infiltration of silver in a porous network of WC. SPS proved to be an interesting alternative technology to produce fully dense Ag-WC composites with a significantly refined microstructure. Break-only test, which simulate arcing conditions in real switching devices, were carried out to investigate the microstructure after switching. The effect of the WC particle size and amount of Ag on the Vickers hardness was also studied.

Shaping of alumina microspheres using vibrational droplet coagulation

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The recent growth of interest in uniform microspheres for different applications is what led us to produce spherical ceramic beads of different size and architecture. During the past years many methods have been developed to shape microspheres using different techniques, such as: spray drying^[1], extrusion dripping^[2], vibrational droplet coagulation^[3] and rotating disk atomization^[4]. In order to obtain uniform microspheres the vibrational droplet coagulation is selected in the course of the research. Thereby the technique enables the shaping of microspheres with different architectures varying from dense to hollow and core-shell.

The shaping of the alumina microspheres can be influenced in two manners since both the composition of the ceramic suspension as the process parameters of the technique have an effect on the size and shape. The viscosity of the ceramic suspension consisting of alumina powder and a binder system has a key role in the shaping process. Alginate is chosen to be the binder in the suspension and will cause the solidification of the microspheres due to the ionotropic gelation with a non-monovalent cation in the coagulation bath.^[5] By changing the ratio of both elements it is possible to tune the viscosity of the suspension and the shrinkage of the dried microsphere. Those changes results in microspheres with different dimensions. In addition to the composition of the suspension the shaping process can also be influenced by modifications in the process. The suspension is introduced in a nozzle by incorporation of a feed pressure. By changing the nozzle diameter and architecture it is possible to change the dimensions of the microspheres. Since the shaping process starts with creating a liquid flow through the nozzle, the feed pressure needed has also an influence on the size of the microspheres. The liquid flow is broken up in droplets by application of a vibration with a certain frequency at defined amplitude. This vibration results in the formation of one droplet per hertz of frequency applied to the extruded flow and has also an impact on the size of the created microspheres. After the droplet generation and solidification in the coagulation bath, the microspheres needs to be subjected to a post processing. The wet microspheres have to dry in a controlled way in order to keep the uniform size and shape. After drying, the spheres need to be thermally treated. This treatment has to be optimised to the application in which the microspheres have to be used.

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Mechanical behaviour of porous anisotropic ceramics obtained by freeze casting: porosity gradient effect.

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This work aims to investigate functionally graded and continuously aligned pore structures process by freeze casting. Such technique allows to process eco-friendly porous ceramic with a control of the porosity. When the solvent used is water, ceramic particles are pushed ahead a solidification front for obtaining, after freeze drying and sintering, a lamellar anisotropic structure.

The structure characteristics are governed by several parameters namely the powder and binder content and the freezing rate. One of the objectives was to establish the link between the structural characteristics (porosity rate, gradient of porosity, pore size ...) and mechanical behaviour (compressive strength, strain ...).

The compressive strength typically varies between 6 MPa and 200 MPa and the apparent elastic modulus between 0.2 GPa to 25 GPa. Analyses of the structure before and after compression were used to establish a relationship between the strain or the stress and gradient of porosity observed by X-ray radiography, along the axis of freezing. The porosity gradient appears to be related to the formation of a dense ceramic layer during the first moments of freezing. This would result in a depletion of the slurry's powder content, appearing at the end of the freezing step (top of the sample).

A new protocol has been defined in order to limit and suppress the formation of the dense part. Furthermore, early termination of the freezing has reduced the porosity gradient from 40 to 8%. These samples, more homogeneous, were characterized in terms of their mechanical behaviour. It has been observed that the reduction of porosity gradient leads to a reduction of the fracture strain and an improvement in mechanical properties.

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Zirconia nanocrystals: effect of metal precursor on the crystalline phase and surface chemistry

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Zirconia can adopt three different crystalline phases, i.e. monoclinic, tetragonal and cubic. Zirconia (ZrO_2) is used in numerous applications depending on its crystalline phase, e.g. cubic ZrO_2 is applied in oxygen sensors, tetragonal ZrO_2 is used as high performance transformation-toughened ceramics and can catalyze ethanol formation from syngas, while monoclinic ZrO_2 will catalyze isobutanol formation from syngas and is important for gate dielectrics and bioactive coatings. The cubic and tetragonal phase are not stable at room temperature, but they can be stabilized by reducing the crystallite size of ZrO_2 below 30 nm can have the same effect.¹

The autoclave synthesis of metal oxide nanoparticles (NPs) through the benzyl alcohol route is readily described in literature.² In this work, we used the same benzyl alcohol route but via a microwave-assisted solvothermal treatment. Here, the same result – cubic ZrO_2 NPs – is obtained as in the conventional method. However, the microwave treatment makes it possible to reduce the reaction time from 2 days in the autoclave to 4 hours in the microwave.

Furthermore, we demonstrate the possibility to use this microwave-assisted solvothermal treatment to synthesize both pure monoclinic or pure cubic ZrO_2 NPs by solely changing the precursor. The reaction mixtures were analyzed by GC-MS. These results lead to the formulation of different reaction mechanisms, depending on the used zirconium precursor.

The as-synthesized ZrO_2 NPs (cubic or monoclinic) are small in size (3 – 10 nm), aggregated and show a low dispersibility. Aggregate-free NPs are generated through a surface-functionalization with long chain ligands, providing stabilization in apolar solvents via steric hindrance. Solution 1H NMR was used to study the details of this post-modification step and the surface chemistry of the resulting aggregate-free NPs. This led to the conclusion that a different surface chemistry is obtained depending on the used precursor.

So, we found an energy-efficient method to synthesize pure monoclinic or cubic ZrO_2 NPs, free-from agglomeration, by changing the zirconium precursor. Moreover, the difference in precursor lead to a difference in reaction mechanisms and NP surface chemistry.

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Rapid synthesis of fine-grained Ti₂SnC produced by spark plasma sintering

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Fine-grained Ti₂SnC was successfully synthesized and densified by spark plasma sintering (SPS) starting from pure elemental Ti, Sn and C powders. The complete reaction route was characterized using interrupted sintering experiments. Ti₂SnC was the predominant phase at 1325°C, with a minor amount of remaining Sn. At lower processing temperatures, Ti-Sn intermetallics and TiC were present, whereas the decomposition of the MAX phase into Sn and TiC was observed at higher temperatures.

Synthesis of hierarchically porous ZSM-5 catalyst for MTO

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Greening up industrial chemical processes can provide beneficial effects for industry and society. By enhancing the stability, selectivity or activity of catalysts, both economic and environmental benefits can be obtained. Industrial catalysts are traditionally used in packed beds of pellets. In order to enhance the mass- and heat transfer in the reactor, the particles can be downsized, leading to an increase of pressure drop. The use of macroporous support materials allows to avoid this kind of trade-off. By using innovative three-dimensional fiber deposition (3DFD) technology, a robocasting technique, the catalyst support material can be built up layer by layer allowing an enormous freedom of design of the porous support [1,2]. By changing the architecture of the support, the mass- and heat transfer in the catalyst bed can be altered in function of the application [3,4].

In this work, robocasted samples with different architecture were synthesized and coated with ZSM-5 zeolite. A wash coating technique was used to deposit a ceramic layer on the support structures. By optimizing the composition and process steps of the wash-coating, a stable and homogeneous coating of the active material could be obtained. The coated samples were compared for the methanol to olefins (MTO) reaction in order to investigate the influence of the architecture of the support on the catalysis.

It has been shown that 3DFD technology offers a good tool for the rapid shaping of metallic and ceramic powders. By coating the support structure with a layer of ZSM-5 zeolite the structure was made catalytically active. This coating however showed poor stability under ultrasonic conditions. By adding a milling step in the procedure and adding 1wt% of inorganic binder the adhesion was increased significantly. The optimized coatings could withstand the high temperatures, chemicals and mechanical stress during catalytic testing and regeneration cycles. The catalytic testing has shown that the architecture of the support material has a significant impact on both the stability and selectivity of the MTO reaction.

Robocasting could become an interesting tool for other applications as well, with different coatings or by robocasting new materials. In future work also highly reproducible ceramic structures will be made such as silica or alumina 3DFD structures.

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Ordering of TiO₂ nanoparticles to mesoporous structures

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Mesoporous titania is a cheap, non-toxic photocatalyst that can play an important role in for example hydrogen generation from water splitting, -air and water purification. Furthermore, porous titania is already used as a catalyst in different industrial processes, such as the recovery of elemental sulfur from waste gases.

A generally applied synthesis strategy for this kind of materials is the soft-templating approach in which hydrolysis and condensation reactions around micelles of the template result in the formation of an amorphous network of titanium dioxide^[1]. This is followed by a thermal treatment to remove the template and crystallize the TiO₂. The disadvantage of this procedure is the use of high thermal treatment temperatures, necessary to create the photocatalytically active anatase crystal phase, which causes the collapse of the porous structure due to thermal instability of the organic soft template.

A recently developed strategy to synthesize crystalline mesoporous TiO₂ structures consists of first synthesizing TiO₂ nanocrystals and their subsequent ordering by addition of a micelle forming surfactant that contains a functional chemical group that can chemically anchor to the nanoparticles^[2]. This approach was used for the research depicted in this presentation. Different types of TiO₂-nanocrystals were tested, as this method can be combined with nanocrystals with interesting morphologies, like nanosheets with highly active (100) facets.

Two different surfactants were used, the commercial available pluronic P123 and a self-synthesized PDMA-b-PS block copolymer. We were able to obtain crystalline anatase TiO₂ exhibiting a surface of 230 m²/g and a high degree of crystallinity. The obtained powders with the different surfactants and nanocrystals were investigated for their photocatalytic activity by following the degradation of methylene blue under UV-light.

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Surface Chemistry of Colloidal Nanocrystals a solution NMR analysis

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The colloidal synthesis of nanocrystals in apolar media results in hybrid systems combining a solid inorganic core and a ligand shell of organic material. Apart from stabilizing the colloid by steric hindrance, these ligands play a crucial role during synthesis and they determine the physicochemical and physical properties of the nanocrystal. This makes the understanding of the binding of ligands to colloidal nanocrystals a key element of nanocrystal research. In this talk, a solution NMR toolbox, comprising 1D NMR spectroscopy and different 2D techniques like DOSY and NOESY, is proposed for the analysis of nanoparticle ligands. First, the toolbox is introduced by means of nanoparticle/ligand systems with tightly bound ligands, such as CdSe/oleate or PbSe/oleate. Next, a number of case studies are presented, which result in a comprehensive picture of the surface chemistry of metal sulfide and selenide nanocrystals in apolar media. In a final part, it is shown how this conceptual insight in the surface chemistry provides a deeper understanding of ligand exchange reactions.

Monitoring tools coupled to a numerical model dedicated to a faster drying of refractory concrete linings

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Keywords: “Refractory concrete”, “castable drying”, “monitoring tools”

A safe drying of refractory castables bonded with hydraulic cements is the main challenge during the first heat up of refractory lining furnaces. During the drying step, the water contained in the castable changes into vapour. The steam pressure inside the material rises with the temperature rising and can become higher than the tensile resistance of the material. It leads to some lining damages such as failures, cracks and in the most extreme cases to an explosion.

The present work is focusing on establishing some critical parameters such as heating rate, steam pressure, slab shape, coupled to concrete properties such as tensile resistance or the mixing water in order to try to optimise the drying critical step.

First, the data obtained from monitoring drying tests realised with large concrete samples (55*55*10 cm³) were collected. The slabs were instrumented with several thermocouples and wave guides overcome of acoustic emission sensors. The slabs weight has been also measured during tests. The heating was conducted in a pilot furnace allowing semi-industrial heating conditions, from room temperature to a furnace temperature of 450°C. Three different heating rates were applied: 0.25°C/min, 0.5°C/min and 1°C/min. The results obtained with a LCC castable showed a critical temperature zone during the drying, between 100°C and 200°C, where the steam pressure increased without steam evacuation outside of the slabs. The steam evacuation seemed to start when the last water drop is transformed into vapour. The temperature of the ebullition end inside the material seemed to be linked to the heating rate of the furnace. This relationship between both parameters and the knowing of the tensile resistance of the material in the critical temperature zone allows an estimation of critical drying rate for this LCC concrete.

A second critical zone linked to the slab thickness can also be established thanks to a 2D numerical model. This one is able to simulate the change of the temperature, steam pressure and humidity in function of the starting humidity, the heating rate and the slabs dimension. One of the main results obtained from this model is the numerical steam pressure change in function of the slab thickness. The maximum of the steam pressure is located close to the hot surface.

The use of monitoring tools dedicated to the castables drying coupled to the development of a numerical model will be a powerful method in order to optimise a safe drying period during the first heat up leading to energy and time savings.

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How to handle LiMn₂O₄ as a cathode material for lithium ion batteries

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LiMn₂O₄ is an excellent candidate cathode for Li-ion batteries due to its high voltage plateau, non-toxicity and good rechargeability. In this study, chemical solution deposition routes are being explored for the synthesis of LiMn₂O₄ thin films because of their low cost, the excellent stoichiometry control and the high deposition rate.

Aqueous and non-aqueous precursor solutions are synthesised and successfully spin- or spraycoated onto different substrates, such as Si/SiO₂, eventually coated with TiN or Pt. Through an elaborate study of the precursor chemistry, deposition and processing parameters, crystalline LiMn₂O₄ was obtained either in air or N₂ ambient at low temperature. The stoichiometry, crystallinity, morphology and electrochemical properties are studied via Raman, XRD, SEM and Cyclic Voltammetry, respectively. Additional information about the precursor residues on films is obtained by Grazing angle Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy. In this way, the key process parameters of each coating could be related to the properties of the LiMn₂O₄ film such as surface roughness, density, porosity, thickness, crystallinity and electrochemical properties. Eventually, LiMn₂O₄ was successfully deposited on an electrolyte material (LLT) to test the properties of a possible half-cell, in view of a possible future device.

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Influence of composition on thermal behaviour of Stainless Steel /Zirconia composites

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The ever increasing demand for pieces capable of withstand severe conditions has stimulated the development of composites which combine mechanical strength, in particular fracture toughness, with corrosion resistance, refractoriness and wear resistance, properties which are not present simultaneously in traditional pure materials and alloys. This is the case of ceramic/metal composites.

Research into composites that incorporate ceramic particles as a reinforcement phase, has aimed to enhance the wear resistance, hardness, and elasticity of pure metals. Advanced composites have a potential for application as engineering materials in energy technology and auto mobile industry. The ceramic phase having a small coefficient of thermal expansion and high hardness provides the thermal stability and abrasive resistance, while, the metallic phase improves the thermal and electrical conductivity, impact resistance and toughness.

On the other side, due to the brittleness and low fracture toughness of ceramics, their applications are limited in high and low temperature structural parts. In order to overcome this problem, a ductile second phase can be introduced into their structure in order to act as a barrier for the crack propagation and to increase tensile strength of the ceramics. The most important mechanisms for the improvement of fracture toughness in the cermets are bridging of the crack, energy depreciation by the plastic deformation and shearing of the ductile metallic phase [8].

In this work, composites with variable relative levels of 316 Stainless Steel and Stabilized Zirconia, obtained by high-energy milling process, were prepared and the thermal behavior of each composition was studied, to determine the influence composition and heating rate on linear retraction rate and total retraction. Dilatometric analyses were performed for composites materials with different proportions of Stainless Steel and Zirconia with the objective of understanding the behavior of Stainless Steel/ Zirconia layers during sintering.

Differential scanning calorimetry tests were performed and the influence of zirconia on phase transformation of Stainless Steel was determined.

Electrochromic windows elements elaboration by ultrasonic spray pyrolysis

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Some metallic oxides present electrochromic property which means that their optical transmittance can be modified by the effect of insertion or desinsertion of electrical charges.

These materials may be integrated in architectural windows with the aim to control the light incoming or outgoing from a building (Smart windows). This technology is one of the key of energy saving in domestic application in the future.

This work demonstrates the possibility to realise “all inorganic” electrochromic layers by the way of Ultrasonic Spray Pyrolysis (USP) technique. USP allows the deposition of the different layers and can be a low cost alternative to vacuum deposition techniques currently applied for commercial applications.

The efficiency of WO₃¹ and NiO² is shown as optically active.

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Fouling resistant ceramic nanofiltration membranes for water treatment

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Keywords: Ceramic nanofiltration membranes, Antifouling, Grafting, Model foulants solutions, Real stream waters

Water is an extremely valuable commodity for society but also for industry. Therefore, adequate processing of water (cleaning and recycling) is essential. Membrane technology can be a flexible and viable long-term strategy for treatment of water. However, widespread use of membranes for water treatment is hindered due to fouling caused by the impurities present in the water. Particularly, natural organic materials (NOM) strongly reduce the membranes performance especially for NF membranes. Fouling is a major drawback and an unsatisfactorily resolved problem of membrane technology up to today, not only for water treatment but for all other membranes applications.

Fouling of membranes (both polymeric and ceramic membranes) is caused by surface properties including hydrophilicity and charge. Therefore, we have developed smart surface functionalization to decrease the fouling tendency. In this study, focus is on two approaches for surface functionalization of ceramic NF membranes using Grignard reagents and Phosphonic acids. Both techniques are applied to commercial TiO₂ NF membranes manufactured by Inopor GmbH Germany. Systematic studies were carried out to explore the potential of surface functionalization for fouling reduction, the correlation between foulants chemical properties and membrane surface, and ultimately how the type of functionalization relates to the fouling resistance. This way, a methodology to tailor surface functionalization on TiO₂ nanofiltration (NF) membranes is being developed, to reach a desired set of properties to diminish fouling.

The fouling tendency of the membranes (with and without fouling-resistant functionalization) was tested by doing filtrations using model foulant solutions and real waters. Experimental results revealed that grafting of NF TiO₂ membranes by the mentioned techniques definitely decreases their fouling tendency. Importantly, methyl functionalized membrane (Grignard method) exhibited a significantly lower propensity to foul throughout all measurements using model foulants solutions. All the results shown can be elegantly explained taking into account the chemical structure of functionalized membrane and foulants. Moreover, antifouling tendency of this membrane has proved also excellent in different real streams : real surface water, olive oil waste water and produced water.

Monitoring of refractory concrete drying

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Keywords: *hydraulic setting refractory concretes, hydraulic setting castables, drying, monitoring.*

In recent decades, there has been an increasing use of hydraulic setting refractory concretes. By comparison to refractory brick, these materials often enable significant saves in time and money while improving thermomechanical performances. However the use of these concretes is subjected to major risks of cracking and even explosion during the first heating of the plant. Indeed, the rise in temperature causes an increase of the vapor pressure in the material that is function of the evaporation and diffusion rates of the free water. Therefore, the heating ramp must be sufficiently low to keep this pressure under control and avoid mechanical damages. Currently, the drying of the concrete is performed following empirically determined heating curves. No heating protocol based on scientific arguments and no suitable tools for monitoring and controlling the drying have been proposed. Therefore, this study aims to better understand the drying behavior of hydraulic setting refractory concretes by using suitable tools for in-situ monitoring (Acoustic Emission techniques, pressure sensors, stress and humidity). A better understanding of the behavior of these materials during heating would help defining optimum heating curves and then improve the materials performances while reducing the energy consumption.

Microwave assisted synthesis of mesoporous titania and relevant surface interactions with dye molecules.

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Titania is the most widely studied and applied material for photocatalytic applications. Enhancing the surface area of a titania catalyst could significantly increase its activity as photocatalytic reactions typically proceed on or near the surface of the material. Conventional soft template synthesis routes like EISA or hydrothermal syntheses are time consuming processes, including long aging times and inefficient heating procedures. [1] Our work focuses on the use of microwave assisted methods for the synthesis of mesoporous titania. Microwaves can directly couple to the solvent molecules used during synthesis, making it possible to create very fast heating, avoiding slow heat transfer through different materials (air-metal-solution) typical for hydrothermal routes. In order to achieve the highest increase in photocatalytic activity, the material needs to be highly crystalline. In case of titania nanoparticles synthesized through hydrothermal methods, it has been shown before that microwave irradiation improves the crystallinity of the nanoparticles and allows reducing synthesis temperature and time [2], therefore it is also possible that microwave irradiation improves the degree of crystallinity in mesoporous titania.

Results and Discussion

Mesoporous titania samples are prepared using an EISA and a hydrothermal route, with and without microwave irradiation. Rietveld analysis was used to determine that microwave irradiation was indeed able to enhance the degree of crystallinity in mesoporous titania. Other characteristics like specific surface area, particle size and band gap energy of the materials, were not affected by the microwave treatment. The different synthesis routes lead to materials with a different surface chemistry. This could be revealed by using FTIR to determine the surface groups. The isoelectric points of the materials were also investigated and are depended on the synthesis route.

Conclusions

Using microwave irradiation it is possible to enhance the degree of crystalline material in mesoporous titania without a negative effect on other characteristics of the material. Different synthesis routes lead to materials with different surface properties which is important for specific applications of the materials.

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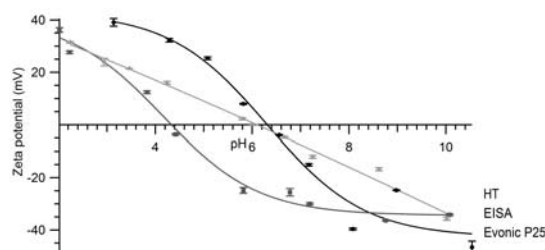


Figure 1: Zeta potential curves of the reference material Evonic P25 and the samples prepared by a hydrothermal route and an EISA route.

Amorphous and perovskite $\text{Li}_3\text{xLa}(2/3)\text{-xTiO}_3$ (LLT) solid electrolyte for all-solid-state lithium-ion batteries by aqueous chemical solution deposition

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In order to tackle the challenging energy storage problem, Lithium-ion (Li-ion) batteries are promising candidates due to their high power and energy density. However, lifetimes and safety of contemporary batteries are limited due to the use of a liquid electrolyte. All-solid-state Li-ion batteries, where liquid electrolyte is replaced by introducing a solid electrolyte such as LLT, could circumvent these issues. Although a lot is known about LLT powders, little is known about (thin) films of this material.

In this study, thin films of LLT have been deposited by spin coating on TiO_2 as an anode. An aqueous citrate / nitrate precursor solution was synthesized. Thermal analysis showed decomposition of the precursors was completed by 600°C . in-situ XRD studies of the LLT thin film crystallization, indicated that prolonged heating at 700°C was required to obtain tetragonal Perovskite LLT on TiO_2 . SEM and ATR-FTIR showed that dense thin films with thicknesses ranging from 50 to 400 nm have been formed with negligible organic contents. Finally, the ion conductivity of the amorphous LLT film was assessed by impedance spectroscopy, indicating a Li-ion conductivity in the range of 10^{-8} S/cm.

Although the conductivity should be further improved, this study indicates that aqueous CSD is a promising route for preparing $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ solid Li-ion conductor compared to other deposition methods.

ALIGNMENT OF ZIRCONIA DURING ELECTROPHORETIC DEPOSITION IN A STRONG MAGNETIC FIELD

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Key Words: EPD, Zirconia, Magnetic alignment, Reactive sintering, Toughness

It has been shown in literature that the mechanical properties of ceramic materials can be tailored by crystallographic texturing i.e. by giving the ceramic grains a preferred orientation. One method to achieve ceramic texturing is during colloidal processing by aligning the suspended particles in a strong magnetic field and retaining this alignment in the green body. The alignment is possible for equiaxed particles with a pronounced anisotropy in the magnetic susceptibility. It is most effective at high fields and for the larger particles. As the microstructure coarsens during sintering the aligned large particles will gradually consume the smaller ones and thus the texture in the material is enhanced by this grain growth process. In the current work, electrophoretic deposition (EPD) of zirconia in a high field of 17.4 T was investigated. When EPD is performed in a strong magnetic field, the charged particles, before deposition, rotate to an orientation to minimize the system energy. Attempts to align tetragonal zirconia particles have not proven successful, not even in the highest fields. However, monoclinic zirconia was successfully textured with significant alignment in the green samples. Monoclinic zirconia was aligned with its (100) plane perpendicular to the magnetic field direction. Textured tetragonal zirconia was developed by reactive sintering of undoped pure monoclinic zirconia and co-precipitated 8 mol% yttria-stabilized zirconia. The tetragonal zirconia inherited the alignment of the monoclinic zirconia used as a precursor and aligned with its (001) plane perpendicular to the magnetic field direction. The (001)-oriented 3Y-TZP showed anisotropic toughness with a high value along the [001] direction. In other words, the cracks generated at the Vickers indentation tips do not propagate equally parallel and perpendicular to (001) direction, as shown in Fig.1.

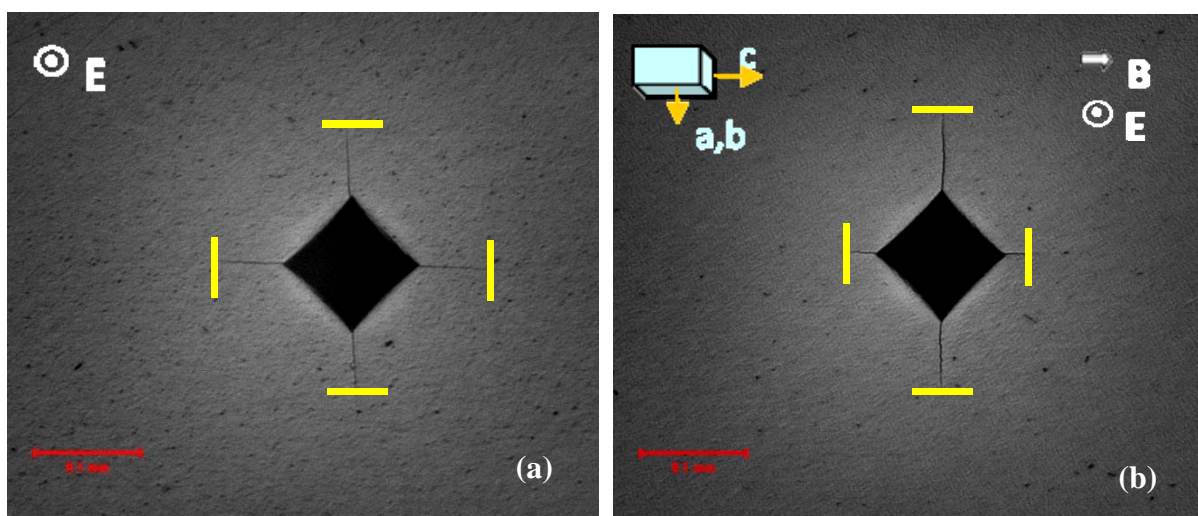


Figure 1 – Vickers indentations and crack propagation in a tetragonal zirconia deposited outside (a) and inside (b) a strong magnetic field.