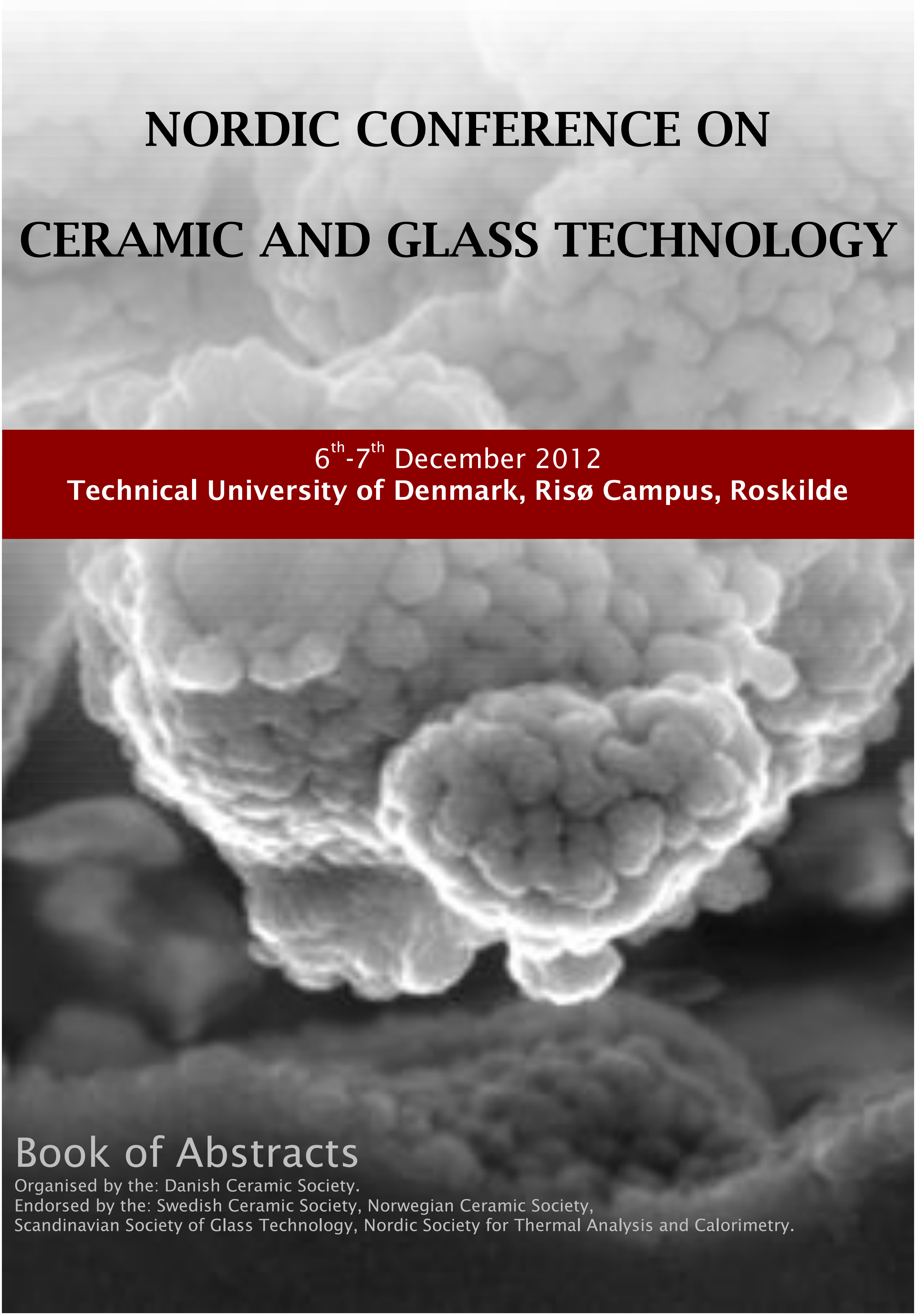

NORDIC CONFERENCE ON CERAMIC AND GLASS TECHNOLOGY

6th-7th December 2012

Technical University of Denmark, Risø Campus, Roskilde

Book of Abstracts

Organised by the: Danish Ceramic Society.
Endorsed by the: Swedish Ceramic Society, Norwegian Ceramic Society,
Scandinavian Society of Glass Technology, Nordic Society for Thermal Analysis and Calorimetry.

An investigation on chemical and mechanical properties of a silicate based glass for planar IT-SOFC application

Poster session, Exhibition and LUNCH

Presenter: ABDOLI, Hamid[1], Parvin Alizadeh[1], Dino Boccaccini[2], Karsten Agersted[2]

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A hermetic sealing is of high priority in development of planar solid oxide fuel cells (SOFCs). Glass and glass–ceramics have been extensively studied due to the wide range of properties available through modification of the composition. The objective of the this work was to investigate the thermo-physical, chemical, and mechanical properties of a silicate based seal glass in the vicinity of ferritic stainless steel as metallic interconnect. Thermal expansion, wetting behaviour and crystallization tendency of synthesized glass were evaluated by thermal analysis routs. To investigate the crack healing capability of the sealing glass, technique of Vickers indentations was applied on heat treated and polished sample. Due to enough residual glass, seal material showed good capability to heal cracks after reheating to 800°C. Glass powders were formed as tape and joined with metals to make sandwich type samples at different times (0.5 and 1h), atmospheres (air, argon, Vacuum) and applied compressive pressures (100 and 500 g/cm2) at 850° C. After sealing, samples were cooled to 800° C and aged for 100h. Microscopic studies were conducted on the interfaces assisted by EDS chemical analysis. The results showed good stability with no gaps and porosity along the interface, however, more severe reaction was observed at the edges of joint samples, where oxygen from air is in excess. To inhibit the edge degradation, surface of metal parts were modified by peroxidising and coating application methods. Electrophoretic deposition technique followed by redox sintering was used to stabilize MnCo2O4 powder as protective coating. To elaborate the interfacial modification, mechanical tests were conducted on samples by double cantilever beam testing. Results showed good interfacial bonding, where stable crack propagation was observed through the glass layer.

Kinetic analysis of sintering CGO in air

Poster session, Exhibition and LUNCH

Presenter: Dr. AGERSTED, Karsten (DTU, Energy conversion)

Gadolinium-doped ceria powder (Rhodia, HSA) was sintered with two additives, Mn2O3 and Cu2O3, to promote densification and grain growth during sintering and compared to sintering the pure powder with and without applied load. The densification kinetics was characterised and it seems that grain boundary mobility was activated by the added promoters, even at earlier stages.

Processing Porous Powders into Hierarchically Porous Macroscopic Adsorbents for Gas separation

Plenary session III

Presenter: Prof. BERGSTRöM, Lennart (Dept. of Materials and Environmental Chemistry, Stockholm University)

The use of porous materials in industrially important applications, e.g. gas separation and purification, require that the porous material is assembled into mechanically strong and hierarchically porous macroscopic structures such as structured monoliths and laminates. Ideally for gas separation applications, the structured adsorbent should combine high volumetric efficiency, good mass and heat transfer, an even gas flow distribution, rapid adsorption/desorption kinetics, and structural integrity. We will demonstrate a versatile binder-less approach to structure zeolite monoliths with high CO2 uptake capacity, high CO2 selectivity and rapid uptake and release kinetics and high mechanical strength. A figure of merit will be defined to evaluate the performance of such structured adsorbents comparisons with recently published porous carbons and metal organic frameworks will be made. In addition, we will show how the zeolite material can be structured in to a membrane support for zeolite films. Finally, the concepts of adsorption and diffusion, mass and heat transfer will be combined in a discussion of the optimal porous architecture and geometry of structured adsorbents.

Characterization of Silicon Nitride using Advanced Thermal Analysis Methods

Plenary session II

Presenter: Dr. BLUMM, Jürgen (NETZSCH-Gerätebau)

In the production of modern high-tech ceramics, a green body is frequently manufactured of ceramic powder and additives (binder, sintering aids). This material is then shaped into green body. The green body is converted into the final product through thermal treatment at high temperatures. The temperature program during the firing process, especially during the binder burnout and in the sintering phase, has a lasting effect on the subsequent characteristics of the product. To optimize the temperature program during firing, the thermophysical properties such as the density change, the specific heat and the thermal conductivity have to be known. Pushrod dilatometers have been used for decades to investigate length changes of ceramics during sintering. Using measurement results achieved at different heating rates and an advanced thermokinetic analysis software (NETZSCH Thermokinetics), one can analyse the kinetics of the sintering process and calculate temperature profiles for various scenarios, e.g. for optimum densification of the material. Thermogravimetric measurements can be used to analyze the binder burnout and decomposition reactions. Differential scanning calorimetry (DSC) can be used to measure the specific heat. Additionally, differential scanning calorimetry allows for the analysis of phase transition temperatures and enthalpy changes. Laser flash is a well-established method for determination of the thermal diffusivity. By combining the results of all measurements, it is possible to determine the thermal conductivity of the material and to predict the temperature gradients in ceramic parts by employing finite element simulations. Presented in this work is a thermophysical properties characterization of various advanced ceramics between room temperature and 2300°C (2600 K). Silicon Nitride green bodies were prepared and analyzed with the different methods. Furthermore, simulations have been carried to analyze the temperature gradients in a ceramic green body during thermal treatment.

Nanoporous silica membranes with high hydrothermal stability

Poster session, Exhibition and LUNCH

Presenter: Dr. BOFFA, Vittorio (Aalborg University)

Despite the use of sol-gel derived nano-porous silica membranes in substitution of traditional separation processes is expected leading to vast energy savings, their intrinsic poor steam-stability hampers their application at an industrial level. Transition metal ions can be used as dopant to improve the stability of nano-porous silica structure. This work is a quantitative study on the impact of type and concentration of transition metal ions on the micro-porous structure and stability of amorphous silica-based membranes, which provides information on how to design chemical compositions and synthetic paths for the fabrication of silica-based membranes with a well accessible and highly stabile nano-porous structure.

Dissolution Studies of Borate Glasses

Plenary session I

Presenter: BROW, Richard University of Missouri-Rolla

The dissolution behaviour of simple borate glass compositions, including those in the Na2O-CaO-B2O3 system, will be reviewed. In general, borate glasses dissolve congruently in water, and in static conditions. Because boric acid is a weak acid, the dissolution processes generally increase the pH of the solutions. The glass dissolution rates in water decrease by two orders of magnitude with increasing [Na2O+CaO]-contents up to about 30 mole% total modifier content, then increase with further modifier additions. These rates mirror other properties associated with the ‘borate anomaly’ and so indicate a greater chemical stability for glasses with tetrahedral borate structures. Raman studies of solutions indicate an increase in the relative concentrations of tetrahedral borate anions with increasing solution pH. Phosphate anions, either in solution or released from borate glasses during corrosion, will react with other ions released from the glass to form phosphate precipitation phases. Ca-containing borate glasses have been developed for biomedical applications and an amorphous Ca-phosphate layer forms on these glass surface, then converts to hydroxyapatite (HAp). The kinetics for HAp formation exhibit similar compositional dependences as noted for the water dissolution rates. In general, borate glasses convert to HAp much more rapidly than do silicate glasses, creating opportunities for new biomedical applications for borate-based glasses. Rare-earth containing glasses react in aqueous environments to form solid solutions of REPO4 that have potential optical applications.

Laser green shape milling of complex shaped ceramic parts: the Evomill process.

Forming and firing ceramics

Presenter: Dr. CAMBIER, Francis (BCRC: Belgian Ceramic Research centre (member of EMRA))

Compared with conventional methods, laser machining of ceramics has various advantages and drawbacks: it is a noncontact method with excellent precision but the matter removal rate is low and the presence of recast layer gives bad surface qualities. In laser machining of ceramics at the green state, particles absorb the radiation, heat up the surrounding organic matter which burns, producing a gas jet. This expanding gas drags the green matter outside the treated area. Unfortunately, the quality of machining remains poor and the machining depth hardly exceeds a few mm. A proprietary new method, carried out on green parts, has been developed (Evomill) to overcome those limitations. An additive phase dispersed within the green body, selectively absorbs the incoming laser radiation. This phase degrades by thermal ablation and the rapid expansion of the resulting gases explodes locally a small area of the green body. The process is very fast, accurate and no depth machining limitation has been noticed. After the machining step, the secondary phase is fully degraded by a thermal treatment before the sintering. The sintered parts are free of defects and fully dense. Complex cm-sized 3D parts like dental prosthesis, micro-turbines and micro-devices have been successfully processed.

Defect thermodynamics and transport in Ce0.8PrxTb0.2-xO2-d and use of ceria in oxygen permeation membranes

Membrane transport properties

Presenter: Dr. CHATZICHRISTODOULOU, Christodoulos (DTU Energy Conversion)

The oxygen non-stoichiometry of Ce0.8PrxTb0.2-xO2-d was measured as a function of oxygen activity, aO2, by coulometric titration and thermogravimetry. A non-ideal solution model allowing for a linear d-dependence of the partial molar enthalpy for the reduction of the dopants was necessary to account for the measured d(log aO2) data. The influence of co-doping on the reduction of Pr and Tb was further investigated by XANES at the L3 edge of Ce, Pr and Tb. A symmetrically blocking electrochemical cell with local ionic and electronic probes was employed for the determination of all the Onsager coefficients of transport in Ce0.8Pr0.2O2-d. The cross coefficients are significant for oxygen activities between 10-3 and

Dense Ceramic Membranes for Hydrogen Separation Prepared by Solid-State Reactive Sintering

Filter and membrane development

Presenter: COORS, W. Grover’
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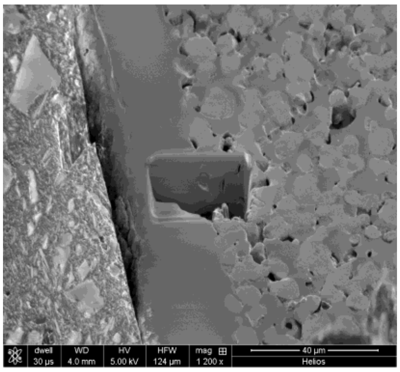
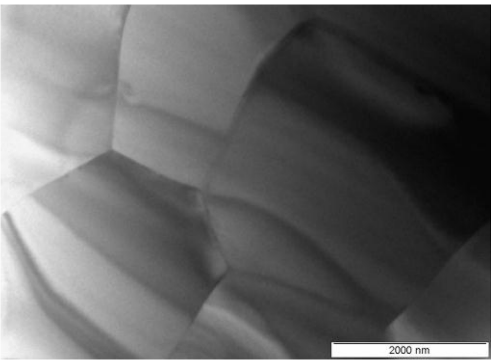
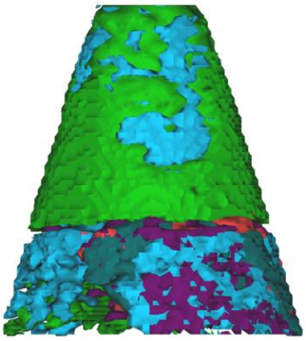
b Colorado School of Mines, Golden, CO 80401, USA

Fabrication of dense ceramic membranes for hydrogen separation on an industrial scale requires a radical new approach to making thin polycrystalline films. The requirement for nearly perfect hermeticity cannot be achieved by traditional ceramic sintering methods, because high sintering temperatures for long durations are necessary. With solid-state reactive sintering (SSRS), the desired protonic ceramic phase is formed in-situ from stoichiometric precursor oxides rather than pre-calcined powders. In this way, solid-state reaction and sintering occur simultaneously to produce a very high-density, phase pure protonic ceramic electrolyte at modest temperatures. Hydrogen separation membranes fabricated by SSRS with the protonic ceramic BaCe0.2Zr0.7Y0.1O3.d (BCZY27), will be described. Dense membranes of BCZY27, 25 ▯m thick, were deposited on the outside surface of porous Ni/BCZY cermet support tubes. The closed-one-end tubes, measuring 1.0 cm in diameter and 25 cm in length, have been tested in tube-in-shell reactors for many thousands of hours under a wide range of atmospheres and operating temperatures typical of industrial processes of commercial interest.

Detailed analysis of the ceramic microstructure of membranes before and after operation will be presented. Focused Ion beam (FIB) was used to prepare TEM specimens from specific areas of interest: electrolyte membrane, electrolyte/porous support interface, and porous support. FIB has become an invaluable tool for evaluating ceramic microstructure relative to the functional macrostructure of working membranes. The left-hand image shows a typical FIB cross-section of the electrolyte membrane and cermet support. The center image shows a typical TEM image of the dense ceramic membrane. Atom Probe Tomography (APT) was used to study cermet macrostructure in the region of the interface, as shown in the right-hand image.







Characterization of lithium phosphorous oxynitride (Lipon) thin films for lithium ion batteries

Poster session, Exhibition and LUNCH

Presenter: CHRISTIANSEN, Ane S., STAMATE, Eugen, HOLTAPPELS, Peter (Department of Energy Conversion and Storage, Technical University of Denmark, Fredrikborgsvej 399, P.O. Box 49, DK-4000 Roskilde, Denmark)

The increasing demand on microelectronic components has made the development of compact, all-solid-state thin film batteries highly interesting. Lithium phosphorous oxynitride (Lipon) is an amorphous Li+ ion conductor that has a very high electrochemical stability of up to 5.5 V. This makes it a strong candidate for electrolyte in compact, flexible and high-power-density batteries needed for various miniaturized electronic devices, such as sensors, circuit boards, medical implants, etc. The Li+ conductivity is highly dependent on the structural disorder induces by the nitrogen incorporation in the Li3PO4 network, but despite extensive research this dependence is not yet well understood. The objective of this work was to correlate the plasma and thin-films properties using detailed plasma diagnostics by mass spectrometry and optical emission spectroscopy. Experiments were performed using RF magnetron sputtering of a Li3PO4 target in N2 atmosphere onto a Au-coated Si substrate. The influence of RF power and N2 pressure on reactive species formed in the plasma was investigated in direct correlation with morphology and electrochemical properties of the Lipon films. Impedance spectroscopy was used to determine the Li+ conductivity from 7x7 mm2 Au/Lipon/Ag cells and the microstructure was investigated using focused ion beam scanning electron microscopy. Mass spectrometry revealed a high degree of nitrogen decomposition at lower pressures (5 mTorr) and low power (100 W). At these conditions a thin dense layer with a conductivity of 2.2*10-6 Scm-1 was obtained, while at high N2 pressures the Lipon growth resulted in “volcano-shaped” structures with a lower conductivity. Further studies are necessary to find proper ways to increase the conductivity and explain its mechanism in relation to nitrogen.

Upscaling the synthesis of Li-ion battery cathode materials: critical to getting EVs on the road

Materials for energy storage and conversion

Presenter: Dr, DAHBI, Mohammed
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The development of larger, more efficient, cheaper and necessarily "greener" Li-ion batteries (LIBs) for electric vehicle (EV) and stationary energy-storage applications continues to present an apparently insuperable challenge. For example, we are still only half way towards achieving the USABC goal set in 1993 of 200 Wh/kg for the gravimetric energy density for an EV-battery system. In this context, the absence of an ideal cathode material with a sufficiently high energy-density is arguably the most serious bottleneck. There are several underlying reasons for this; not least, the availability and cost of raw materials. Several millions of tons/year of the active cathode material will be need if we are to achieve our long-term goal of a world-wide transition from ICEs to EVs.

A significant breakthrough came with the development of polyanion-based cathode materials; typically, phosphates and silicates: e.g., LiFePO4 [1] and Li2FeSiO4 [2]. These materials are, in principle, expected to be both cheaper (neglecting the economy of the process) and safer than conventional LIB transition-metal oxide cathode materials, such as LiCoO2 and LiMn2O4. A negative feature of these materials is, however, their poor electronic conductivity – a problem which is normally addressed by reducing particle-size into the nano-range and promoting ion conductivity by the use of various particle-surface coatings. Judicious doping strategies, often based on DFT model calculations, are also desirable for these essentially electronically insulating materials. Arguably the most promising cathode materials for large-scale applications involve the Li-M-SiO4 family of silicates, typically Li2FeSiO4. Recent advances in our efforts to address the challenge of scaling up the synthesis of these materials will be reported, giving examples taken from our use of solid-state (see Fig. 1), solvothermal, precipitation, solution, microwave and combustion methods.

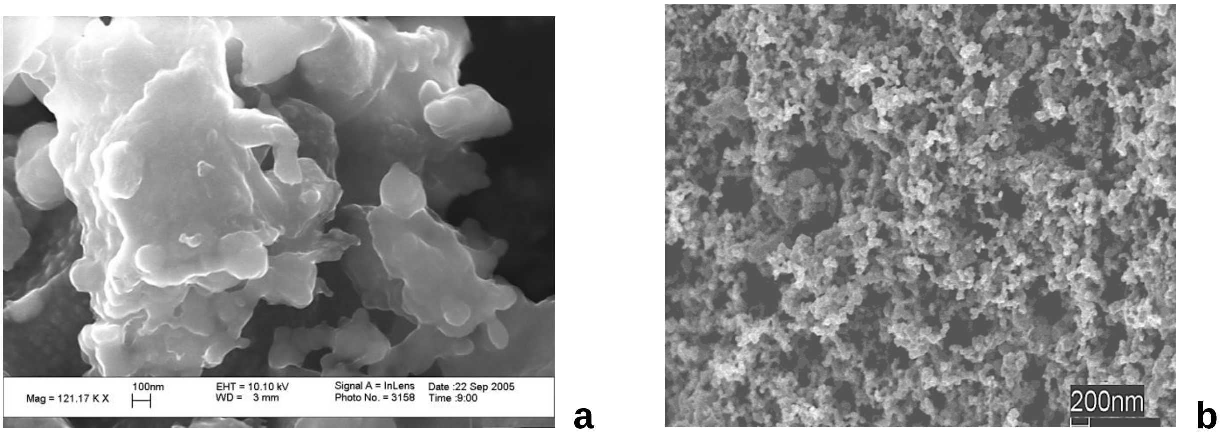

Fig. 1 TEM images (ca. same scale) of less desirable (left) and ideal (right) Li2FeSiO4 microstructures for an EV-battery cathode material: (a) 12 hours mixing/grinding gives a low surface-area material with poor battery performance; (b) 2 months mixing/grinding gives a highly porous, high surface-area material with good battery performance. This material is made by a solid-state synthesis technique.

This work has been supported by the Global Climate and Energy Project of Stanford (GCEP), the Swedish Energy Agency (STEM), VINNOVA and the Swedish Science Research Council (VR).

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[2] A. Nytén *et al.*, *Electrochem. Commun.*, 7, 156 (2005).

Ceramic based water filters for bacteria and virus filtration

Filter and membrane development

Presenter: Dr, GRAULE, Thomas; Michen, Benjamin

Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, 8600 Dübendorf Switzerland

Water purification is necessary to prevent the spread of different diseases, which are caused by water-borne germs like bacteria, protozoa, and viruses. The germs can be separated from the water by a physical process, there the contaminated water is passing a porous medium like a filter.
This study is focused on the physical separation of germs from water with ceramic based filters. Diatomite was used as raw material for the filter production. Diatomite, also known as diatomaceous earth, is composed of the remains of unicellular aquatic plants called diatoms, which enclose themselves in a shell of silica. The perforated open porosity makes them attractive for filter applications. The filters were produced either by slip casting or by extrusion.

Compared to the well established slip casting process used for water filtration since more than 20 years, extrusion is a near net shape process developed during the last years. It could be shown that a significant reduction of production time as well as material consumption is possible. Both auger and ram extrusion techniques could be applied to achieve high quality bacteria filters removing more than 99,9999 % of bacteria having a size from 0.3 to 1 micrometer.

To further extend the application of diatomite based ceramic water filters to virus removal a special modification process of the filter structure was applied. Virus filtration (MS 2 bacteriophage; size 25 nm) with an efficiency of more than 99,99 % could be achieved. Modification of the porous ceramic surface was achieved by incorporation of nanosized inorganic particles composed of zirconium oxide or yttrium oxide.

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Hydrogen permeable asymmetric La28-xW4+xO54+3x/2 membranes

Membrane transport properties

Presenter: Dr. GIL, Vanesa (NTNU (Norway)//currently DTU-Risø campus)

Development of new high temperature ceramic materials exhibiting high proton and electron conductivity as well as the processing technologies to shape these into hydrogen permeation membrane systems used for production of intermediate olefins/aromatics are of potential interest to the petrochemical industry. High-temperature mixed conductors in the lanthanum tungstate family, La28-xW4+xO54+3x/2 (LWO), with La/W ˜ 5.7-5.3, are currently among the most promising materials for extraction and/or purification of hydrogen from syngas or other hydrogen containing mixtures or for catalytic selective hydrogenation. In order to assess the true potential of these materials as hydrogen-permeable membranes, it was important to measure hydrogen permeation directly on thin film (25 µm) asymmetric membranes, as permeation estimates from conductivity data often are based on simplified models and permeation measurements on thick samples can conceal possible surface kinetic limitations. Details of the processing conditions for asymmetric La28-xW4+xO54+3x/2 (x=1.22, La/W=5.6) based thin film membranes as well as the high temperature (700-1000 C) hydrogen permeation results as a function of temperature and feed gas conditions will be presented.

Chemically Induced Strain in Electroceramics

Plenary session I

Presenter: Prof. GRANDE, Tor (NTNU)

Composition in most conventional ceramics is fixed by nature and strain in such materials can only be induced due to phase transitions or crystallographic anisotropy. Both these phenomena may cause microcracking at a critical grain size, but may also open up for transformation toughening or toughening based on ferroelastic domain switching. Here we will discuss chemically induced strain in electroceramics, which may cause mechanical failure of electrochemical devices. Recently, the phenomenon of chemical expansion in mixed electronic and ionic oxide materials such as La1-xSrxCoO3-d due to changes in the valance state of Co as a respond to changes in temperature or partial pressure of oxygen has been well documented. We will demonstrate by our recent investigations that the chemical expansion is strongly anisotropic in materials with lower than cubic symmetry. Less known is the considerable chemical expansion associated with the hydration of proton conducting oxides. A phenomenological treatment of the phenomena will be discussed, and some recent X-ray and neutron diffraction data will be presented.

Processing of asymmetric membranes for oxygen gas separation

Forming and firing ceramics

Presenter: Dr. GURAUSKIS, Jonas (Norwegian University of Science and Technology)

Mixed ionic-electronic conducting membranes for oxygen gas separation are attracting a lot of interest due to their promising potential for oxygen and syngas production. Apart from intrinsic membrane material properties, the membrane arrangement may enhance significantly the oxygen flux values, emphasizing the need to establish consolidation routes to obtain reliable membrane assemblies with desired geometry and controlled microstructure. In this work, the processing conditions for producing La0.2Sr0.8Fe0.8Al0.2O3-delta (LSFAl) perovskite based membrane for oxygen separation were evaluated. Asymmetric membranes consisting of a dense thin (˜20µm) functional layer on a thick porous support were prepared. The porous support was fabricated by a tape casting technique, employing LSFAl powder obtained by solid-state reaction and using carbon black as a pore former. The functional membrane layer was deposited on one side of the porous support, employing the same composition powder obtained by spray pyrolysis.

Optimization of the targeted tape casting and thin film deposition suspensions with desired colloidal properties will be reported. Adjustment of substrate porosity as a function of processing parameters, structural performance and permeability will be discussed.

Complex mechanical moduli of a supercooled liquid measured over 14 decades in frequency

Glass science and structure

Presenter: Dr. HECKSHER, Tina (Roskilde University, DNRF Centre Glass & Time)

When a liquid is cooled continuously without crystallizing the viscosity increases enormously; the liquid 'stiffens' while remaining in a (possibly meta-stable) equilibrium liquid state. Such supercooled liquids display viscoelastic behaviour, and elastic moduli measured in these liquids thus become complex and frequency-dependent. The time scale of the transition from solid-like to liquid-like behaviour is roughly proportional to the viscosity and typically varies 16 orders of magnitude going from the thin liquid above its melting point to the extremely viscous liquid just above the glass transition temperature. Covering such a large dynamical window is an experimental challenge that no single technique can meet. We have successfully matched measurements from six different techniques that together span 14 orders of magnitude in frequency from mHz to THz. Here we present the broadband mechanical spectrum of a silicone oil (tetraphenyl tetramethyl trisiloxane) measured in the temperature interval from 150-400 K. This unprecedented span in frequency and temperature provides a unique possibility to test elastic models connecting the instantaneous elastic moduli to the relaxation time, examine Cauchy relations, follow the relaxation time and the evolution of the spectral features over a wide temperature region.

Technical Ceramics for advanced applications

Plenary session III

Presenter: HEIDMANN, Alexander

The presentation introduces to the world of Technical Ceramics. Outstanding Properties of the material are highlighted to explain the extended field of industrial applications. For a ceramic adapted construction the knowledge of the complex production procedure is required. Therefore different forming operation processes and other steps for formation the final part are shown. Samples of application out of different industries clarify the characteristics of successful use.

Bioactive glasses – from bone grafting to tissue engineering

Glass materials and application

Presenter: Dr. HUPA, Leena (Åbo Akademi University)

In the presentation the bioactive glass research at Åbo Akademi University over the past thirty years will be summarized. The goal of our research has been on understanding how physical and chemical properties as well as bioactivity depend on glass composition. We have studied several series of glasses within a large composition range from 45 to 65 wt% of SiO2. Selected glasses have been studied in vivo as cooperation with research groups at the Faculty of Medicine at Turku University. The focus of the research has been on developing tools for finding novel compositions of bioactive glasses with unique combinations of properties. The manufacturing properties have been expressed with models for viscosity and crystallization characteristics of the glasses. Changes in simulated body fluid and on glasses after immersion have been used to develop models of the in vitro bioactivity of the glasses as functions of the oxide composition. One of the milestones has been the development of glass S53P4, a commercial bone grafting material available as BonAlive®. Also another Åbo Akademi composition, glass 13-93 showing lower tendency to crystallization than traditional bioactive glasses has been studied by several research groups for various applications. The bioactive glass compositions used in clinical applications show high bioactivity, i.e. the glasses start to react and bond to living tissues within a few days after implantation. So far, the clinical applications of glasses deal with non-load bearing applications only. However, during the past years bioactive glasses have been studied intensively as components of composites together with polymers. Using thin fibers or thin-walled highly porous structures increases the surface area of the glasses. Accordingly, the glasses are likely to react rapidly in vitro and in vivo and thus might lose their mechanical strength more rapidly than new bone forms. For these applications the glasses should have a slower bioactivity and higher chemical durability. The need of tailoring glass compositions with desired in vivo reactivity has encouraged us to further develop our understanding of glasses for medical applications. Our latest research deals with development of bioactive glass based tissue engineering scaffolds with controlled ion dissolution to support and enhance osteogenesis, angiogenesis and antimicrobial effect. The results will be applied for tailoring compositions of bioactive glasses with a desired product form and a desired biological effect.

Can liquids in nano-confinement be simple?

Glass science and structure

Presenter: Mr. INGEBRIGTSEN, Trond (Roskilde University)

Liquids near interfaces show rich and complicated behaviour. For instance, a liquid confined to the nano-scale may change its dynamic properties several orders of magnitude compared to the bulk system. Predicting these changes is an important challenge relevant for biological systems, engineered devices, etc. We consider here whether it is possible to apply a recently introduced concept in statistical physics, namely isomorphs [N. Gnan et al., J. Chem. Phys. 131, 234504 (2009)], to the understanding of nano-scaled confined systems. Isomorphs are invariance curves in a liquid's phase diagram, along which certain thermodynamic, all structural and dynamic quantities are invariant in so-called reduced units. We consider also in the framework of isomorphs, a recently established thermodynamic-kinetic-relationship among bulk and confined systems for predicting the dynamic changes induced by the nano-scale confinement.

Experimental methods for measuring on viscoelastic glass-forming liquids

Glass science and structure

Presenter: Dr. JAKOBSEN, Bo (Glass and Time, Department of Sciences, Roskilde University)

A major research aim of the "Glass and Time" group at Roskilde University has over the years been to develop methods for characterizing the viscoelastic behaviour of glass-forming liquids. We review a number of these techniques. The shear modulus [1,2], adiabatic bulk modulus [3,2], longitudinal thermal expansion coefficient [4,5], longitudinal specific heat [6], adiabatic pressure coefficient [7], dielectric relaxation, and physical aging [8] can be measured under identical conditions. Such datasets are unique and provide a possibility for comparing different response function and for testing models. Two examples of results combining the techniques are presented. The characteristic time obtained by different techniques are compared [9], and a prediction from the recently proposed isomorph-theory about the pressure and temperature dependence of the characteristic time is tested [10].

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[3] Christensen and Olsen PRB (1994)
[4] Bauer et al. Non-Cryst. Sol. (2000)
[5] Niss et al. PRE (2012)
[6] Christensen and Dyre, PRE (2008); Jakobsen et al. PRE (2010)
[7] Christensen et al. Non-Cryst Sol. (2011)
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[9] Jakobsen et al. JCP (2012)
[10] Gundermann et al. Nat. Phys. (2011)

Fabrication and Characterization of Proton Conducting Phosphate Electrolytes for Intermediate Temperature Fuel Cell Assembling

Materials for energy storage and conversion

Presenter: Ms. JENSEN, Annemette Hindhede (DTU Energy Conversion)

The worldwide development of fuel cells and electrolysers has so far almost exclusively addressed either the low temperature window (20 - 200 °C) or the high temperature window (600 - 1000 °C). The intermediate temperature window enables the possibility of combining advantages from low and high temperature technologies. Fast electrode kinetics and material stability are key parameters. However, in the intermediate temperature interval there are no proton conductors working satisfactorily. The finding of such electrolytes is an ultimate goal of solid electrolyte research. [1] Certain proton conducting materials are plastic in nature e.g. CsH2PO4, whereas others are not e.g. NdPO4. By combining the materials in a ceramic composite with at least one other component, it is possible that suitable mechanical properties can be reached.

In former work, proton conduction has been demonstrated for ceramic NdPO4-CsH2PO4 composites using EIS. [2][3] Based on the novel ceramic composite a hydrogen cell and hydrogen-air fuel cells has been constructed and operated. Under these conditions proton conduction was confirmed by EMF and thermal stability in fuel cell conditions was confirmed by OCV.

Acknowledgement

Funding for this work is obtained from the Danish National Research Foundation (the Danish-Chinese Center for Intermediate Temperature Proton Conducting systems (PROCON)).

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[2] A. H. Jensen, 3rd CARISMA International Conference on Medium and High Temperature PEM Fuel Cells, Copenhagen, 3 – 5 September 2012, 60 – Poster session
[3] T. Anfimova, 3rd CARISMA International Conference on Medium and High Temperature PEM Fuel Cells, Copenhagen, 3 – 5, September 2012, 65 – Poster session

In-situ techniques for investigation of the role of sintering aids on the preparation of Ce0.9Gd0.1O1.95 multi-layer membranes

Forming and firing ceramics

Presenter: Dr. KAISER, Andreas

Andreas Kaiser *, Aditya Prasad, Søren P. Foghmoes, Nikos Bonanos, Severine Ramousse, Vincenzo Esposito, Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark. * Corresponding author, Tel: +45 46775778, E-mail: dwei@dtu.dk

Asymmetric thin film membranes with CGO (=Ce0.9Gd0.1O1.9-δ) as mixed conducting membrane layer have been investigated for different membrane reactor applications, such as syngas reaction or oxidative coupling of methane. Major issues in the preparation of such asymmetric membranes are: (1) the selection of the suitable materials for support and membrane for each application; (2) optimization of the co-sintering process for the asymmetric structure to avoid defect formation and camber; (3) the selection of suitable sintering additives. For the application in oxidative coupling of methane asymmetric CGO bi-layers (20 µm thin dense membrane of CGO on a 0.5 mm thick porous CGO support) have been produced. Sintering aids were tested to reduce the temperature for full densification of the thin CGO10 membrane layer. In-situ characterization methods were implemented to better describe the role of cobalt oxide as sintering aid on the densification of tape casted CGO multi-layers, to reduce the camber and to optimize the sintering profile. For this purpose two in situ techniques have been combined. Optical dilatometry revealed that shape and microstructure of the asymmetric CGO bi-layer is dramatically changing in a narrow temperature range of less than 100°C (see Fig. 1). At temperatures below 1030 °C, a higher densification rate in the dense membrane layer than in the porous support leads to concave shape. Above 1030 °C the densification rate of the support is dominant, leading to convex shape. At temperature as low as 1030°C the shrinkage rates were similar and flat bi-layers could be produced.

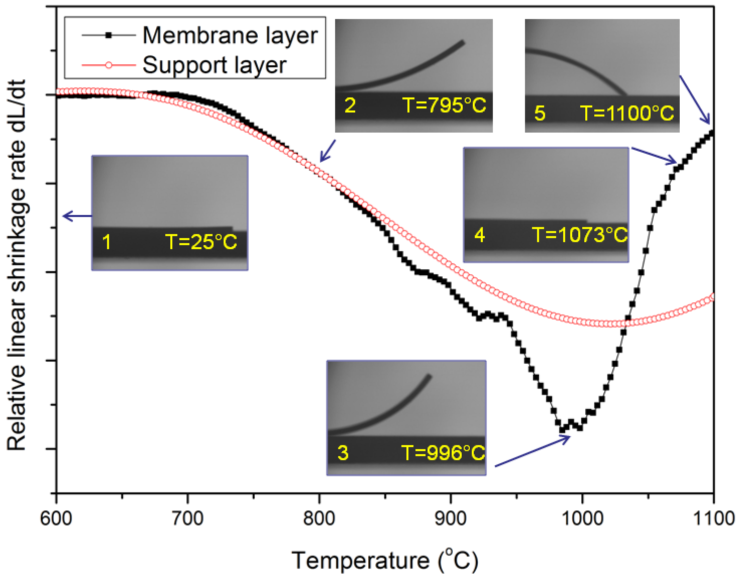

Fig. 1 Relative linear shrinkage rates of CGO tapes: a) dense membrane layer (filled squares) and b) porous support layer (open circles). Inset pictures from optical dilatometry show the shape evolution of the laminated porous/dense bilayer at selected temperatures (dense layer facing upwards).

In-situ van der Pauw measurements on the tape cast support and membrane layers during sintering allowed following the conductivity during sintering. For the dense membrane layer a strong increase in conductivity and in activation energy Ea for conduction was observed between 900 and 1030°C indicating an activation of the reactive sintering process and phase transformation of cobalt oxide (Fig. 2). Isothermal Van der Pauw measurements on the membrane layers at high temperatures after sintering suggested a predominant role of cobalt oxide on the degradation of (total) conductivity in such CGO thin film membranes under operation (Fig. 3).

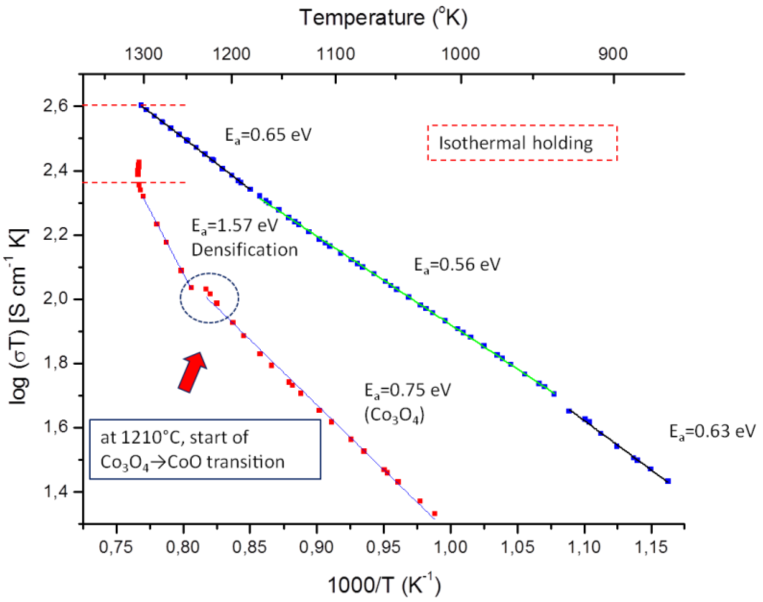

Fig. 2 Arrhenius plot of the conductivity of a CGO "dense" membrane layer with 2 at-% cobalt oxide, measured in-situ by Van der Pauw method during sintering. The thermal cycle included a heating and cooling rate of about 1 °C/min and an isothermal hold at 1030 °C for 4 hours.

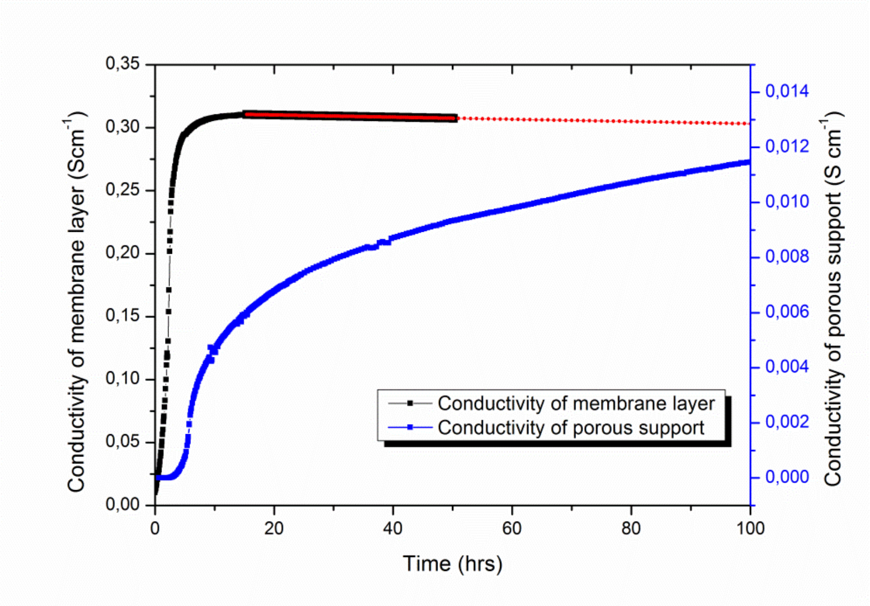

Fig. 3 Time dependence of isothermal conductivity of porous CGO layer (open circle) and dense CGO layer (filled squares) at 1030°C. The first 10 hours show a raise in conductivity due to heat up to final temperature of 1030°C. The thin, dotted line is a linear extrapolation of conductivity (loss) for the membrane layer (resulting in an extrapolated degradation rate of 2.8% over 100hrs).

Single-Side Ion Exchange Strengthening of Holed Float Glass

Glass science and structure

Presenter: Dr, KARLSSON [1,2]Stefan*, [1]Bo Jonson, [1]Marie Johansson, [1]Bertil Enquist
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[2]Glafo AB – PG Vejdes väg 15, SE-351 96, Växjö, Sweden

The fracture strength of oxide glasses is to a large degree influenced by other factors than the inherent strength of the bonds in the vitreous network such as surface defects. Due to the brittle nature of glass, mechanical processing decreases the strength substantially. The aim of this study was to investigate ion exchange strengthening also known as chemical strengthening of commercially available mechanically processed soda-lime-silicate float glass and to compare it with as-received float glass by means of flexural fracture load. The dimensions of the samples were 66±2 x 66±2 mm and two series had 7 mm diamond drilled holes in the centre of each sample while one series was as-received. Ion exchange of sodium ions by larger potassium ions were performed by treating the air-side of a series of samples with a KNO_3:KCl mixture at 450 °C. The flexural fracture load of both untreated and ion exchanged holed samples was measured by means of the coaxial double ring test. The ion exchanged samples showed an arithmetic mean fracture load increase of approximately 160% compared to untreated holed float glass. The drilled hole decreases the arithmetic mean fracture load to approximately 25% of as-received float glass whilst the strengthening effect of the ion exchange improves it to around 65% of as-received float glass.

Durability of Monolithic Silicalite-I Membrane Supports in Aqueous Solution

Poster session, Exhibition and LUNCH

Presenter: Ms. KESHAVARZI, Neda (Departments of Materials and Environmental Science, Stockholm University)

Porous inorganic membranes are used in harsh operating conditions such as strong alkaline or acidic solution which effectively influence their life time and efficiency. The materials properties such as composition and crystallinity, determine the stability of such porous membranes. Exposure time, temperature, pH changes, the medium and its flow rate are parameters that must be quantified to estimate the life time of the material in use. In this work the effect of composition and pH changes in aqueous media, on chemical durability of silicalite-I membrane supports is studied. Pulsed current processing is used to consolidate binder-free silicalite-I membrane supports. Furthermore, the role of different binder compositions, kaolin and colloidal silica, on the chemical durability of silicalite-I membrane supports consolidated by conventional thermal treatment are compared. Static tests are performed at 90 °C by immersing the membranes in strong acid at pH 2.0, intermediate pH 10.6 and alkaline aqueous solutions at pH 13 for duration of one week. The silicon concentration in solution, change of crystallinity, BET surface area, pore size distribution and strength are measured to estimate the durability in the applied caustic conditions. Silicalite-I membrane supports are significantly degraded at pH 13 evidenced by silicon concentrations released into the solution and total loss of BET surface area.

Functional Ceramic and Glass Materials in Solid Oxide Fuel Cells – An overview about state-of-the-art technology and current challenges

Glass materials and application

Presenter: Dr. KIEBACH, Wolff-Ragnar (DTU Energy Conversion and Storage)

Solid oxide fuel cells (SOFCs) are electrochemical devices that produce electricity directly from various fuels, e.g. hydrogen, bioethanol or hydrocarbons. Compared to traditional technologies, SOFCs exhibit high electrical efficiency, low noise levels and reduced CO2 emissions. The excellent load following capability coupled with the ability to co-generate heat and clean electric power should ensure that SOFCs will play an important role in future decentralized, intelligent power grids. The heart of any SOFC is a multilayer ceramic cell, which allows the generation of power by electrochemically oxidizing the fuel. In this presentation, the basic working principles of SOFC will be discussed with focus on the functionalized ceramic materials used. Next to the state-of-the-art materials like yttria stabilized zirconia (YSZ) for electrolytes, Ni/YSZ cermet for anodes and Sr doped lanthanum manganite (LSM) for cathodes, also recently developed high performance materials will be presented. In a SOFC stack, several cells are stacked together to produce enough power for specific applications. Each module's compartments must be sealed, and there must be seals between the modules in a stack so that air and fuel do not leak or mix, resulting in a loss of efficiency or internal combustion. The remaining part of the presentation will give an overview about glass-ceramic sealants, which are used for this purpose, as well as for the requirements and challenges in the developments of these materials.

High-performance porous zirconia nanoceramics with hierarchical heterogeneities

Dispersion and colloidal chemistry

Presenter: Dr. KOCJAN, Andraz (Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden)

High-performance porous zirconia nanoceramics were developed by using a mesoporous powder consisting of about 200-nanometer-sized (d50) spherical particles that are initially composed of ten times smaller, loosely and randomly aggregated crystallites. The green compacts, free of agglomerates, were prepared by either centrifugal casting of weakly flocculated suspensions or by cold isostatic pressing of freeze granulated powders. High densities were achieved in green bodies that exhibited strong hierarchical heterogeneities with bimodal distribution of pores, originating from highly uniform intra- and inter-particle packing. The evolution of pore structure and the formation of necks between the intra- and inter-particles during sintering were studied. It was found that the uniform packing and coordination of aggregated nanoparticles can lead to a superior microstructure with essentially improved properties. We thus demonstrated that the conflicting demand of high mechanical strength in combination with a moderate porosity and low Young`s modulus can be satisfied. As prepared porous zirconia nanoceramics would also offer high pore surface area and beneficial textured surfaces and thus reveals the potentials for using as dental and orthopedic implants.

Sol-gel co-assembly as an alternative method for deposition of ceramic 3D ordered macroporous coatings and polymer/ceramic hybrid coatings

Dispersion and colloidal chemistry

Presenter: Dr. KUBRIN, Roman (Institute of Advanced Ceramics, Hamburg University of Technology (TUHH))

Ceramic 3D ordered macroporous (3DOM) materials widely studied for application as photonic crystals are usually produced by replication of artificial opals. Templates consisting of monodisperse submicron polymer particles are obtained by colloidal self-assembly and can be infiltrated by a ceramic phase in a separate process step via gas phase infiltration (e.g., atomic layer deposition, ALD) or sol-gel infiltration. Recently, it was shown that the sol-gel infiltration could be performed simultaneously with the self-assembly of the opaline templates and, in this way, several drawbacks of the standard fabrication methods of ceramic inverse opal films, such as formation of the drying cracks, can be overcome. Our group works on development of photonic crystals for high-temperature applications. We successfully produced high quality inverse opals made of titanium dioxide by ALD-infiltration at 95 °C. However, ALD of many other ceramic materials, such as yttrium-stabilized zirconia (YSZ) and silica, would require much higher temperatures exceeding the glass transition point of the polymer used for the templates. Here, we report on deposition of 3D ordered silica/polystyrene hybrid coatings in one step by vertical convective co-assembly of PS microspheres and hydrolysed TEOS sol. PS particles later could be removed by calcination in an oven at 500 °C or by a treatment with oxygen plasma. We discuss optical and mechanical properties of the coatings and suggest the ways to further improve their performance.

Foaming of waste cathode ray tube panel glass via CaCO3

Glass materials and application

Presenter: Dr. KöNIG, Jakob (Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark and Advanced Materials Department, Jožef Stefan Institute, SI-1000 Ljubljana, Slovenia)

The disposal of obsolete electrical and electronic equipment has become a global environmental problem. However, with responsible collecting, dismantling and materials separation, majority of materials can be recycled. Cathode ray tube (CRT) glass represents as much as two-thirds of the weight of a TV. In general CRT consists of two types of glasses: barium/strontium containing glass (panel glass) and lead containing glass (funnel and panel glass). In this work we present the possibility to produce high quality foam glass from the recycled lead-free glass. We study the influence of foaming parameters on the characteristics of foam. CRT panel glass was crushed, milled and sieved below 63 um particle size. CaCO3 was used as a foaming agent and was mixed with glass powders using a planetary ball mill. Preliminary results show that milling conditions and particle size have a major influence on the foaming process and resulting density of samples. We investigate the influence of foaming agent concentration on the foaming process, foam density, foam porosity and homogeneity. We demonstrate how milling and foaming conditions affect the foam properties for different amounts of CaCO3. A minimum in the density of foams has been observed with respect to milling time, while homogeneity of foam has been improved with longer milling time. The results also show that for a higher content of foaming agent the milling time needs to be prolonged in order to obtain lower density and homogeneous porosity. Such behaviour is due to stronger interaction between the glass and CaCO3 particles, which lowers the decomposition temperature of the foaming agent.

Development of nanoporous TiO2 and SiC membranes for membrane filtration

Filter and membrane development

Presenter: Dr. KöNIG, Katja (Section of Chemistry, Aalborg University)

Reverse osmosis membranes are increasingly used for the production of drinking water (desalination of sea water or brackish water), for demineralisation of water in industrial processes (boiled feed water, microelectronics production) as well as in food processing and pharmaceutical production. Today´s reverse osmosis membranes are made of polymers; however, these membranes have several technical limitations, for example, low water fluxes and high sensitivity to oxidizing chemicals. Since membrane fouling is still a major problem in reverse osmosis desalination plants, replacement of polymer reverse osmosis membranes by ceramic counterparts would provide higher fluxes and allow more efficient cleaning of the membranes. The aim of this work was to prepare defect-free nanoporous ceramic (TiO2 and SiC) layers on macroporous SiC supports by using electrophoretic deposition and dip-coating. Ceramic powder was dispersed in water and in ethanol, and to increase absolute value of zeta-potential of the particles, different deflocculants (hexadecyltrimethylammonium bromide, polyethylene imine) were added. In parallel, SiC layers were prepared by dip-coating of suspensions containing pre-ceramic polymer allyl-hydridopolycarbosilane dissolved in hexane with addition of submicron SiC particles. In all the cases, after coating step, the layers were dried and heat treated under different conditions. Results show that particle size distribution and thickness of the coatings play an important role in formation of defects. The number of defects decreased with decreasing thickness of the coatings. Furthermore, coatings composed of a mixture of nanosized and submicron SiC powder were more homogeneous than the coatings composed only of nanosized SiC powders. In comparison to conventionally sintered SiC coatings, polymer derived SiC coatings were much better adhered to the surface of macroporous SiC supports.

Lanthanum strontium ferrites as MIEC membranes – Effect of B-site substitution on stability and transport properties

Membrane transport properties

Presenter: Mr. LOHNE, Ørjan Fossmark (Norwegian University of Science and Technology (NTNU))

Oxygen permeable dense ceramic membrane technology for production of syngas (H_2/CO) from natural gas has been an area of significant research for a number of years [1]. The main challenges, still to overcome, are the development of material systems showing sufficient stability at high temperatures and reducing conditions combined with adequate oxygen transport properties. In this contribution we will report on an investigation of the transport properties and stability of $La_{0.2}Sr_{0.8}Fe_{0.8}B_{0.2}O_{3-d}$ (B=Fe, Al, Ti, Ta). Coulometric titration has been performed to obtain oxygen non-stoichiometry as a function of T and pO_2. The results have been fitted to a defect chemistry model and thermodynamic data have been calculated. The stability is assessed from the thermodynamic data and the pO_2 of decomposition and are discussed together with previously reported results obtained by temperature programmed reduction [2]. Electrical conductivity and oxygen transport properties have been obtained by performing electrical conductivity relaxation. The relation between oxygen non-stoichiometry, stability, oxygen transport properties and the effect of the B-site dopant will be discussed.

[1] H.J.M. Bouwmeester, Catal. today, 82 (2003) 141-50
[2] Ø.F. Lohne, et al., Solid State Ion. (2012) In press

Ceria protective coatings for Crofer 22 APU interconnectors for Solid Oxide Electrolysis Stacks

Poster session, Exhibition and LUNCH

Presenter: Dr. MOLIN, Sebastian (Department of Energy Conversion and Storage, Technical University of Denmark)

Solid Oxide Electrolysers (SOEs) are considered as an important component of a future energy system based on a large amount of fluctuating energy sources (i.e. wind power). In SOEC cells, on the oxygen side pure oxygen is generated and on the fuel side highly humidified hydrogen (possibly even pure steam) is present. These atmospheres have relatively high oxygen activities that can cause rapid corrosion of steel interconnectors. It implies that protective coatings might be needed both for the oxygen and for the fuel side. In this work a technology for preparation of protective coatings on Crofer 22 APU steel is presented. Undoped CeO2 is used as a coating material. For both the oxygen and the fuel side, ceria provides a reactive element effect on the oxidation kinetics and hence reduce the thickness of formed oxide scale. Also for the fuel side undoped ceria will provide a barrier between metallic nickel and steel protecting against interdiffusion and austenitisation of steel. Performed work included optimization of ceria deposition method (spin-coating) by tailoring solution composition (concentration, solvent). For developed coatings corrosion kinetics of coated samples is assessed and compared with uncoated samples.

Acknowledgement

Financial support from Energienet.dk through the ForskEL project number 2011-1-10609 “Development of SOEC cells and stacks” is gratefully acknowledged.

Densification and grain growth during sintering of porous Ce0.9Gd0.1O1.95 tape casting layer

Poster session, Exhibition and LUNCH

Presenter: Mr. NI, De Wei (Department of Energy Conversion and Storage, Technical University of Denmark)

Doped-ceria is an important type of materials that offers high stability, tolerance against harsh environments and high ionic and electronic conductivity at high temperatures. Particularly, gadolinium 10 mol% doped ceria Ce0.9Gd0.1O1.95-. (CGO10) has been used as promising electrolyte and cathode barrier layer material for solid oxide fuel cells (SOFC) and flue gas purification, and oxygen transport membranes for high temperatures applications. For most of such applications, CGO10 is typically shaped to be a layer, and part of a multi-layered structure. The ceria may be a thin and dense layer, as e.g. in a SOFC electrolyte and barrier layer, or in a membrane, or a highly porous layer allowing gas flow, which is necessary in a gas purification device or SOFC electrodes. A production friendly and versatile technique for making this kind of layers is tape casting. In ceramic processing, sintering has a great impact on the final microstructures (e.g. density and grain size), since this step usually induces most of the morphological transformations at high temperature. Therefore, detailed understanding of the densification and grain growth mechanisms is the basis for controlling the material microstructure and efficiently optimizing the ceramic properties. The present work investigated the densification and grain growth processes during sintering of porous CGO10 tape cast layer, used as electrolytes in flue gas purification devices. Sintering variables were experimentally characterized and analyzed using sintering constitutive laws. Derived from the sintering constitutive laws, Dorn's method, iso-strain lines approach as well as master sintering curve (MSC) method were employed to determine the densification kinetics. Based on the results achieved, the densification activation energy of porous CGO10 tape was evaluated to be 440-470 kJ.mol-1 in the relative density range of 0.45-0.62. The grain growth activation energy of CGO10 tape during sintering was evaluated to be 430 kJ.mol-1 in the grain size range of 0.1-0.4 .m. In view of the obtained kinetics results, grain-boundary diffusion was identified as the dominant densification mechanism for the porous CGO10 tape investigated. The present work systematically investigated the sintering behaviour of porous CGO10 tape, which contributed to the determination of the fundamental sintering parameters associated with densification and grain growth kinetics.

"Simple"- glass-forming liquids

Glass science and structure

Presenter: Dr. NISS, Kristine (DNRF center "Glass and Time", IMFUFA, RUC)

The glass transition is a universal phenomenon which in its essence is independent of the interactions between the atoms or molecules of the liquid forming the glass. The universal character of the transition has led physicists to believe that there is one underlying simple explanation of the phenomenon. More than 15 years ago the Nobel laureate P.W. Anderson stated that understanding the glass-transition is deepest unsolved problem in solid state physics [1], but a satisfactory explanation is still lacking. Understanding the glass-transition implies understanding the dynamics (eg. diffusion, vibration, relaxation) and the physics in general of the viscous liquid forming the glass. Gasses can to a great extend be understood via the ideal gas model where the interactions between particles are ignored. In crystalline solids the physics can be understood by exploding the periodic nature of the structure. No similar simplification can be made for liquids. Here we need to consider the interaction between the molecules, the kinetic energy and the amorphous structure. This is a challenge to a model systems or a theory explaining the glass transition and the physics of liquids in general.

The "Glass and Time" group on RUC has during the last five years succeeded in identifying a class of simple liquids and a theory for describing these has been developed [2]. This theory, called the isomorph theory, has proven very effective in describing computer simulated liquids with simple interactions (e.g. Lennard Jones liquids). But how useful is the theory when it comes to understanding the physics the liquids we deal with in the laboratory? In 2011 we published the first experimental results supporting the isomorph theory [3]. Here we showed how the relative effect of density and temperature on the glass transition can be understood in terms of the isomorph theory. There are several other predictions of the theory; many of these are directly related to the glass transition. Our current and future experimental work aims at testing these precisions.

[1] Science 267, 1609 (1995)
[2] J. Chem. Phys. 131, 234504 (2009)
[3] Nature Physics 7, 816 (2011)

Shaping of hierarchically porous monoliths by freeze-casting of zeolites

Dispersion and colloidal chemistry

Presenter: Mr. OJUVA, Arto (Stockholm University)

Microporous materials such as zeolites, porous carbon and metal organic frameworks with high surface area and gas uptake capacity are potential candidates for cost- and energy-effective CO2 separation from flue gas. The microporous powders need to be structured into hierarchically porous monoliths to improve the uptake kinetics and to maximize the volumetric efficiency. In this work, we show how a low-cost ice templating process, also known as freeze-casting, can be used to create monoliths in the centimetre range, with gas flow channels and diffusion distances in the lower micrometre range (10-30 µm). Freeze-casting is a versatile shaping method where a concentrated aqueous suspension is frozen with controlled directionality and speed. During the freezing, ice crystals grow directionally and expel the suspended species into a separate dense phase. The ice can then easily be sublimed from the resulting two-phase material, leaving a structured hierarchically porous powder body that can be consolidated by heat treatment to provide a mechanically stable monolith while maintaining the ice-templated macropores in the structure. By controlling the initial concentration and the freezing rate important properties such as wall thickness and pore size can easily be tuned. We demonstrated how freeze-cast suspensions of zeolite 13X powders at an initial solid loading of 40-50 wt% and freezing rates between 0.5 and 5 °C/min resulted in interconnected parallel channels, either lamellar or columnar, with the smaller pore dimension between 5 and 20 µm and a wall thickness between 10 and 40 µm. Measurements of the CO2-uptake at ambient temperature revealed that the zeolite 13X in the monoliths had retained more than 70% of the uptake capacity compared to the starting material. Cyclic tests showed that the actual working capacity in a vacuum swing adsorption process (between 6 and 130 kPa) was 2.8 mmol/g, thus about 60% of the maximum uptake capacity. The kinetics of the adsorption could be modelled with two exponential constants which are related to the initial and latter adsorption step, respectively. This work demonstrates how freeze-casting of microporous adsorbents opens up a new length scale, with macropores smaller than those in extruded ceramics (>1 mm) but larger than the mesoporous in surfactant-templated materials (<50 nm).

Water based processing of LiFePO4 cathode material for Li-ion batteries

Poster session, Exhibition and LUNCH

Presenter: Mrs. ORLENIUS, Jessica (Swerea IVF AB)

Production of electrical vehicles is foreseen to grow substantially in the near future with an accompanying request of up-scaled battery production. Therefore, it is strongly and urgently motivated to apply environmentally sustainable concepts for the manufacture of battery cells including cathodes of Li-based compounds as, for example, LiFePO4. This manufacture is today solvent based, dominating by the use of NMP (N-metyl-2-pyrrolidon), a toxic solvent with potential risks for serious genetic impacts on living species, and PVDF (Polyvinylidene diflouride) as binder. Besides the health/environmental aspects, the processing of toxic chemicals in large scale also renders significant costs to meet national and international regulations that tend to be sharpened by the time. In this study, water based systems for making cathode materials based on LiFePO4 as the active material have been developed and evaluated. Water suspensions with LiFePO4 powder, polymeric binder and carbon black with various compositions were prepared. In contrast to conventional water based tape casting of ceramics, an altered suspension preparation route with low solids loading and a minimum of organic additives (dispersant, binder) was applied. Tape casting was successfully conducted in a tape casting machine with 50-80 µm layers upon aluminium foil. The coated foils were pressed to increase the degree of compaction and thus the conductivity of the cathode layer. Test cells with commercially available lithium metal anode, membrane (separator) and electrolyte, were assembled and tested by charge/discharge cycling. The results showed that the performance in terms of charging/discharging capacity was in the range achieved with cathode material produced by using the established organic system.

Fabrication and tailoring of porous metal membranes by tape casting

Filter and membrane development

Presenter: Dr. PERSSON, Åsa (DTU Energy Conversion)

Tape casting is a well-known ceramic processing technique and as this work will show also applicable for powder metal processing. The metal layers can be manipulated at various steps during the fabrication process, which eventually determines the quality of the end-product. Variable parameters such as the composition of the metal, the pore former addition, sintering inhibitor addition, sintering conditions (temperature, dwell time, and atmosphere) as well as sample size have been shown to have an impact of the final microstructure of sintered metal layers. For some parameters a design of experiment (DoE) approach has been used to investigate the effect on final shrinkage and porosity of the metal layer. By adding only 0.1 wt.% of a specific element to a stainless steel alloy composition the sintering shrinkage of a metal layer was decreased by 40% with a natural increase in porosity. The sintering shrinkage of a metal layer can on the other hand be increased simultaneously as the porosity is increased by increasing the pore former addition. A third way to increase the porosity of a metal membrane is to add a ceramic sintering inhibitor. This work illustrate how conventional ceramic processing techniques can be applied to design and fabricate powder metal layers in a broad thickness range with an in principle tailor-made microstructure. This approach makes it possible to fabricate metal layers with low-cost and up-scalable processes for various applications.

Optimized Synthesis of Foam Glass from Recycled CRT Panel Glass

Glass materials and application

Presenter: Mr. PETERSEN, Rasmus Rosenlund (Section of Chemistry, Aalborg University)

Most of the panel glass from cathode ray tubes (CRTs) is landfilled today. Instead of landfilling, the panel glass can be turned into new environment-friendly foam glass. Low density foam glass is an effective heat insulating material and can be produced just by using recycle glass and foaming additives. In this work we recycle the CRT panel glass to synthesize the foam glass as a crucial component of building and insulating materials. The synthesis conditions such as foaming temperature, duration, glass particle size, type and concentrations of foaming agents, and so on are optimized by performing systematic experiments. In particular, the concentration of foaming agents is an important parameter that influences the size of bubbles and the distribution of bubbles throughout the sample. The foam glasses are characterised regarding density and open/closed porosity. Differential scanning calorimetric data show that panel glass possesses good stability against crystallisation. X-ray diffraction data show that the foaming agents enhance the surface crystallisation of the panel glass. We find that the crystallisation impedes the formation of low density foam glass.

Harvesting of vibrational energy using piezoceramic thick films

Poster session, Exhibition and LUNCH: Materials for energy conversion; Materials performance and testing

Presenter: Dr. RINGGAARD, E.[1]
Co-authors: Dr. ZAWADA, T. [1] ;Dr. GUIZZETTI, M. [1]; Ms. BORREGAARD, L.M. [1]; Dr. XU, R. [1]; Mr. LEI, A.[2]; Prof. THOMSEN, E.V.[2]
1. Meggitt Sensing Systems, 2. DTU Nanotech

Summary:

Energy harvesting spans a large variety of technologies and devices that transform low-grade energy sources such as solar energy, environmental vibrations, thermal energy and human motion into usable electrical energy. Due to the rapid development of ultralow-power electronic devices, the energy harvesting technology has become a very attractive solution for a wide variety of applications, e.g. structural health monitoring, embedded test & evaluation, and condition-based maintenance of roads, buildings, ground vehicles and aircraft. In this work the energy source is vibrations that are transformed by an energy harvesting micro-generator into a usable electrical signal.

The presented energy harvesting micro-generator comprises a silicon cantilever, bottom electrode, PZT thick film and top electrode. The results reported here include generated power versus excitation frequency, and the influence of parameters such as presence and value of a proof mass located at the tip of the cantilever, value of the electrical load resistance and shape of the cantilever (e.g., rectangular or trapezoidal).

Structures of the same shape and dimensions have been manufactured using two kinds of PZT thick film, standard grade and high-performance (pressure-treated) grade, in order to directly compare the performance of the materials. The conclusion of this comparison is that the device based on high-performance PZT thick film produces a constant output power that is significantly higher (by a factor of up to 3.7) than the standard one. This is also supported by the theoretical analysis, where the output power of a flexural energy harvesting device is proportional to $(d_{31})^2/\varepsilon_r$ where d_{31} and ε_r are the transversal piezoelectric charge coefficient and the dielectric permittivity of the piezoelectric thick film, respectively.

Acknowledgment:
The support of the Danish National Advanced Technology Foundation through the ELBA project (ELiminating BAtteries - energy harvesters for integrated systems, contract no. 036-2009-1) is gratefully acknowledged.

From the nano- to the macroscale - Mechanical properties of hierarchically structured biological and biomimetic materials with high ceramic content

Plenary session III

Presenter: Prof. SCHNEIDER, Gerold A. (Hamburg University of Technology)

Many biological materials are hierarchically structured from the nano- to the macro-scale in a sometimes self-similar way. There are lots of papers published including very detailed descriptions of these structures at all length scales however investigations of mechanical properties are most often focused on either nanoindentation or bulk mechanical testing characterizing properties at the smallest or largest size scale. Interestingly, there are hardly any investigations that systematically interconnect mechanical properties of different length scales. Hence, in this presentation hierarchically structured biological materials with high mineral content are ordered according to their hierarchical levels and measured properties are attributed to them. This offers the possibility to gain insight into the mechanical properties on different hierarchical levels even though the entire biological materials were tested. On the other hand we use data of one material, namely enamel, where mechanical properties were measured on every length scale. Indentation and focused ion beam microbar and micropillar tests were used on the smallest lengths scales whereas classical bending and compressions tests were applied for bulk enamel. In the second part of the presentation different processing methods to synthesize hierarchical materials are introduced. The focus is on dense mechanically strong polymer/ceramic-materials. It will be shown, that still there is a lack in a synthetic engineering material displaying a true hierarchical structure. A newly developed multi-step processing route to obtain an anisotropic 2-level hierarchical composite will be presented. It comprises polymer-encapsulated ceramic particles as building blocks for the first level, followed by a spouted bed spray granulation for a second level and finally directional hot pressing to anisotropically consolidate the composite. The achieved microstructure following this approach reveals a nacre-like brick-and-mortar hierarchical structure with distinct mechanical properties on each level. It opens up a completely new processing route for even a large scale production of hierarchically structured composites, giving prospects to future studies on structure-properties relationships.

Predicting the Viscosity of Multicomponent Glass-Forming Liquids

Glass science and structure

Presenter: Prof. SMEDSKJAER, Morten M. (Aalborg University)

The quantitative design of glassy materials with tailored properties is a longstanding problem in the glass science community. One of the most technologically important properties is the shear viscosity, since all stages of industrial glass production require careful control of shear viscosity. Here, we show that topological constraint theory holds the key to understanding the temperature and composition dependence of the viscosity of glass-forming liquids. Using this approach, we derive detailed topological representations of soda lime borate and borosilicate systems that enable the accurate prediction of glass transition temperature and liquid fragility. The implications of the glass topology are discussed in terms of both the temperature and thermal history dependence of the atomic bond constraints and the influence on relaxation behaviour. We also present a phenomenological model offering an improved description of the composition and temperature dependence of the shear viscosity of multicomponent liquids, for which the existing analytical models currently do not apply. The model predicts the isokom temperatures of 7141 viscosity measurements for 760 different compositions with a root-mean-square error of only 6.55 K.

Environmental and quality analysis of aqueous tape casting

Poster session, Exhibition and LUNCH

Presenter: Dr. STIERNSTEDT, Johanna (Swerea IVF AB)

Ceramic tapes are traditionally produced by tape casting using organic solvents. The use of organic solvents has been questioned due to health, environmental and fire hazard risks. The use of water-based tape casting can reduce these problems. There are however other questions associated with water based tape casting: the drying is slower and can cause cracking, air bubbles can be entrapped, and in some cases there can be problems with wetting. These problems can be handled by controlling by controlling the colloidal and rheological properties and using a system with high solids loading. For two reasons it is possible to have high solids loading in water based tape casting; firstly, there are more efficient dispersants available, and secondly, it is possible to use latex binders that do not increase the viscosity in the same way as soluble binders. This higher solids loading decreases the amount of water that needs to be dried and it decreases the risk of cracks. The number of air bubbles is minimized by addition of de-foaming surfactants and by careful handling of the slurry. The wetting can be improved by choosing a more hydrophilic carrier film. We have analyzed tape casting slurries in terms of dry content and rheology, and tape quality. Environmental aspects have been studied using a life cycle assessment approach. We have shown that water based tape casting gives high quality tapes and a significantly lower environmental impact.

Glass fiber transporting daylight into our homes

Glass materials and application

Presenter: Dr. STåLHANDSKE, Christina (Glafo)

Sunlight is what most living organisms have adapted to during evolution. The usage of sunlight in indoor environments has energy advantages and results in improved well-being compared to artificial light. Parans has developed a system transporting sunlight from outside to within. Their system is based on a plastic fiber for guiding the light. The drawback with this fiber is an altered spectrum and losses limiting the range to 20 m. A glass fiber can be designed to have better spectral properties and longer range. The application possibilities would be greatly enhanced and could include larger buildings and underground structures. Glafo together with Acreo, Parans and Uppsala University are developing a suitable glass fiber which could transport sunlight 3-4 times as far as the plastic fiber in use. The aim is to prove that the glass fiber is appropriate and could be produced to a competitive price. The project covers establishing an adequate glass composition, drawing of glass fibers and applying these in Parans system. Two different demonstrators using the glass fiber in a modified system are planned. Akademiska hus will make an installation in one or their real estates in Göteborg. The glass fiber will be evaluated both as a single fiber and installed in the demonstrator.

Preparation, microstructural and electrical characterization of co-doped SrTiO3 materials.

Presenter: Dr. SUDIREDDY, Bhaskar Reddy (Department of Energy Conversion and Storage, Denmark Technical University)

Lanthanum and niobium co-doped strontium titanate (Sr1-3x/2LaxTi0.9Nb0.1O3; x =0, 0.005, 0.01 and 0.02) powders were prepared through mixed oxide route by heat treating the oxide mixture at 1300oC for 4 h in air. Phase analysis of resultant compounds using X-ray diffraction showed Ti-oxide impurity phase at no or low amount of La doping. The observed impurity peak disappeared after sintering at 1450oC for 10 h in either oxidizing or reducing atmosphere. Sintering behaviour in reducing atmosphere was studied using dilatometry and an increase in sintering rate and sintered density was observed with an increase in La doping amount. Microstructural observations showed a marginal decrease in the grain size with an increase in the La doping amount when sintered in air, whereas significant increase in grain size was observed when sintered in reducing conditions. Phase and compositional analysis showed small amount of Ti-oxide phase at all amounts of La doping in samples sintered in reducing atmosphere. Significant increase in the dc electronic conductivity was observed with an increase in La doping content in the compounds sintered in reducing atmosphere. The results show flexibility in tailoring the microstructure and electronic properties, which strengthen the potential for these materials as electrode materials for solid oxide cells.

E-glass crystallization behaviour

Glass science and structure

Presenter: Mr. SVENSON, Mouritz (RISØ), Ms. PEDERSEN, Liisa Julie (Institute of Geography and Geology, University of Copenhagen)

A study of the extend of thermodynamically stable and metastable behaviour of six E-glasses during long term heat treatment (3 months) has been performed. By comparisons between crystalline phase assemblages of the glasses and thermodynamic calculations of their equilibrium phase assemblages indications on crystallization behaviour are found.

Metastable behaviour is identified by deviances from calculated equilibrium phase assemblages and different crystallization conditions are indicated from these comparisons. The metastable behaviour is sought explained by mechanisms of phase separation in residual glasses and crystallization kinetics of the glasses during heat treatment.

Shape distortion and thermo-mechanical properties of SOFC components from green tape to sintering body.

Poster session, Exhibition and LUNCH

Presenter: TEOCOLI, Francesca (Risø-DTU)

Sintering of ceramic materials is a critical process, especially when the components are shaped as multi-layer. From the green stage to the densification stage , the effects of organic additives removal, solid state diffusive phenomena, and either differential expansion or contraction of the layers can be critical on the final shape leading also to failure, delamination etc. In this work, a tape-cast bi-layer structure for CGO and YSZ-(Sc) was studied during the thermal processing from debinding to sintering. The bi-layered samples underwent several phenomena of shape instabilities and deformation due to debinding, differential shrinkage behaviour and to a potential interfacial reaction between the two materials. To analyse the phenomena, shrinkage of SOFC components single layers and bi-layered samples were measured in-situ by optical dilatometry. The densification mismatch stress, due to the strain rate difference between materials, was calculated using Cai’s model. Camber (curvature) development for in situ co-firing of a bi-layer ceramic green tape was investigated. Analysis of shape evolution from green to sintered body was carried out using thermo-mechanical analysis techniques.

Preparation of Stable Pt-Clay Nanocatalysts for Self-humidifying Proton Exchange Membrane Fuel Cells

Materials for energy storage and conversion

Presenter: Dr. WENJING, Zhang (RISØ campus, Technical University of Denmark)

One of the critical challenges in making proton exchange membrane (PEM) fuel cells commercially viable is the inability of Nafion (the most used PEM) to conduct protons at low water content level. Both external humidifier and physical seal of the fixture in commercial products increase the cost and complexity of the whole system. Therefore, we have designed a novel Pt-clay nanocatalysts and developed a Pt-clay/Nafion nanocomposite PEM to significantly enhanced proton conductivity without any external humidification. Monolayer of Pt nanoparticles of diameters of 2-3 nm with a high crystallinity were successfully anchored onto exfoliated nanoclay surfaces using a novel chemical vapour deposition process. Chemical bonding of Pt to the oxygen on the clay surface ensured the stability of the Pt nanoparticles, and hence, no leaching of Pt particles was observed after a prolonged ultrasonication and a rigorous mechanical agitation of Pt-clay in the Nafion solution during the membrane casting process. Planar and hygroscopic clay reduced fuel crossover and balanced the water content. In situ water production for humidification of the dry membranes without any external humidification was characterized by a combined water uptake and FTIR analysis of the as-prepared membrane after a single cell testing without using electrodes. The power density at 0.5 V of a single fuel cell made of a Pt-clay/Nafion nanocomposite membrane was 723 mW/cm2, which is 170 % higher than that made of a commercial Nafion 112 membrane of similar thickness.

Structural Dependence of Physical Properties in Sodium Boroaluminosilicate Glasses

Glass science and structure

Presenter: Dr. ZHENG, Qiuju (Aalborg University)

Boroaluminosilicate glasses have found applications in many fields. The extent and nature of the mixing of network formers like SiO2, B2O3, and Al2O3 play an important role in controlling the macroscopic properties. To understand the structure-property correlations in these glasses, we study a series of sodium boroaluminosilicate glasses with various [Al2O3]/[SiO2] ratios to access different regimes of sodium behaviour. We determine dynamic properties, elastic moduli, and hardness of these glasses. The results reveal an existence of local minimum for density, fragility index, Young’s and shear moduli, and hardness around [Al2O3]-[Na2O]=0. Moreover, there exist three compositional response regions for elastic moduli and hardness. These results are explained in terms of topological constraint theory.