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RAUL VÄLBE

Developement of ionic liquid composites by sol-gel method for elaboration of industrial nano- and microstructures

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Developement of ionic liquid composites by sol-gel method for elaboration of industrial nano- and microstructures

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

I. **Välbe**, **Raul**; Tarkanovskaja, Marta; Mäeorg, Uno; Reedo, Valter; Hoop, Andres; Kink, Ilmar; Lõhmus, Ants. Elaboration of hybrid cotton fibers treated with ionogel/carbon nanotube mixture using sol–gel approach. *Central European Journal of Chemistry*. **2014,** [accepted].

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III. **Välbe**, **Raul**; Mäeorg, Uno; Lõhmus, Ants; Reedo, Valter; Koel, Mihkel; Krumme, Andres; Kessler, Vadim; Hoop, Andres; Romanov, Alexey E. A novel route of synthesis of sodium hexafluorosilicate two component cluster crystals using BF4- containing ionic liquids. *Journal of Crystal Growth*. **2012**, 361, 51–56.

IV. Järvekülg, Martin; **Välbe**, **Raul**; Jõgi, Jakob; Salundi, Aigi; Kangur, Triin; Reedo, Valter; Kalda, Jaan; Mäeorg, Uno; Lõhmus, Ants; Romanov, Alexey, E. A sol–gel approach to self-formation of micro-tubular structures from metal alkoxide gel films. *Physica Status Solidi A – Applications and Materials Science.* **2012** 209(12), 2481–2486.

Other papers in related field:

V. Jarvekulg, Martin; **Välbe**, **Raul**; Utt, Kathriin; Timusk, Martin; Tätte, Tanel. Tailoring Sol-Gel Transition Processes for the Design of Novel Shape Metal Oxide Materials. In: Functional Oxide Nanostructures and Heterostructures. *MRS Proceedings Volume 1256E*: **2010,** MRS Spring Meeting; San Francisco, USA.

VI. Kuusik, Ivar; Tarkanovskaja, Marta; Kruusma, Jaanus; Reedo, Valter; **Välbe**, **Raul**; Lõhmus, Ants; Kisand, Vambola; Lust, Enn; Kukk, Edwin; Nõmmiste, Ergo. Near threshold photodissociation study of $EMIMBF_4$ vapor (**2014** submitted to *Journal of Chemical Physics*).

VII. **Välbe**, **Raul**, Katsetades ioonsete vedelikega, arvesta, et klaasanum võib tulemustesse lisada ka "mäekristalle", **2012** EFS aastaraamat, Tartu (in estonian).

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Author's contribution

I. Synthesis of hybrid materials. Responsible for characterization of obtained materials. Creation of the bibliographical background, carrying out the main part of experiments and writing the manuscript. Corresponding author in pre-revision processes.

II. Creation of the bibliographical background and writing the part of the manuscript. Responsible for experimental work. Synthesis of hybrid materials. Corresponding author in pre-revision processes.

III. Generation of ideas and elaboration of methodologies for conducting experiments. Synthesis and characterization of two-component cluster crystals. Creating the bibliographical background and writing the manuscript. Responsible for preparation of the manuscript and corresponding author in pre-revision processes. Preparation of experimental work of tuning the shape and size of the gel sheets rolled. Responsible for preparation of the manuscript and corresponding author in pre-revision processes.

IV. Preparation of experimental work of tuning the shape and size of the gel sheets rolled. Responsible for preparation of the manuscript and corresponding author in pre-revision processes.

ABBREVIATIONS AND SYMBOLS

ATR	attenuated total reflectance technique
BMIM	1-butyl-3-methylimidazolium
BF_4	tetrafluoroborate
DMPA	2,2-Dimethoxy-2-phenylacetophenone
DMIM	1-decyl-3-methylimidazolium
DSC	differential scanning calorimetry
EDX	energy-dispersive X-ray spectroscopy
EMIM	1-ethyl-3-methylimidazolium
Et	ethyl
FT-IR	Fourier transformation infrared spectroscopy
FIB	focused ion beam
HRMS	high resolution mass spectrometry
IL	ionic liquid
LMWG	low molecular weight gelators
MTICl	1-methyl-3-[3'-triethoxysilyl)propyl]imidazolium chloride
NMR	nuclear magnetic resonance spectroscopy
R	water/alkoxide molar ratio
RTIL	room temperature ionic liquid
SEM	scanning electron microscope
TEOS	tetraethyl orthosilicate
TGA	thermogravimetry

Ionic liquids are marked as [cation][anion], e.g. [EMIM][BF_4]

PREFACE

In today's technology, essentially micro- and nanotechnology is constantly looking to create materials with better properties. Synergy between different phases of the materials (liquid-solid) may influence the properties of the final product significantly. By definition, hybrid material is a system which consists of inorganic, organic, or both types of components which are generally uniformly distributed on a scale of less than 1 μm in a homogeneous mixture [1].

The main problem for alternative technologies for combining liquids into a solid is a fundamental contradiction between the liquid and solid mechanisms where improving one typically diminishes another. Nevertheless, materials' advantageous liquid state turns out to be an impediment for applications in devices which need stable solid state shaping. In addition, it is very important for industry to find alternative materials and technologies to design novel hybrid materials.

The main theme of the work – ionic liquids, which are chemically relatively inert, they have excellent temperature resistance and ionic conductivity. Due to ability to solvate different compounds ionic liquids have attracted the attention in organic synthesis as an alternative reaction media, and in preparation of different composites. Modifications of materials with ionic liquids have been in the focus of a rapidly growing number of studies in the last decade [2]. The immobilization of ionic liquids within organic or inorganic matrices makes it possible to take advantage of their unique properties in the solid state, thus circumventing some drawbacks related to shaping and risk of leakage. Also, for many applications there are frequently a need for immobilizing ionic liquids on solid matrices which are consistent with ionic liquids' liquid-like dynamics to avoid leakages and miniaturization impediments. The new type of materials is called ionogels. Sol-gel synthesized ionogels combine the properties of the two systems (oxide and ionic liquid) intermingled at nanometer scale. In other words, by combination of ionic liquid and metal alkoxides it is possible to create new nano-fine metal oxide porous cross-linked systems, which have practical applications in various fields (e.g. solid electrolyte membranes, selective absorbing material, optical components and catalyst carrier – section 3). In creation of such materials ionic liquids are used as nano-pore templates inside a host matrix.

The thesis is related to the new direction in several important research fields – chemistry, materials science and nanotechnology in design of modern materials with controlled shape and size. The motivation of this study is grounded for the long lasting working experience of the work related persons, using the sol-gel method in development of novel oxide materials [3;4;5;6]. Based on current *know-how* it is efficient and effective to extend the research to new class of materials – ionogels [7] thereby including the clarification of their cognitive and practical applications. The main objective in the theoretical part of the work is to find synergy using different imidazolium based ionic liquids and gain knowledge of sol-gel technology. The experimental section focuses

primarily on the explanation of stability and greenness of ionic liquids, synthesis of different shape and size metal oxide materials, which for the first time combines sol-gel method with self-formation by film rolling, synthesis of homogeneous metal alkoxide/ionic liquid gels, and the use of the obtained mixture to functionalize textile. The preparation of ionogels by sol–gel processing has attracted much attention, because the final hybrid materials combine properties of both inorganic matrix (thermal and mechanical stability) and the ionic liquid (plasticizer agent and ionic conductivity).

The work was carried out in University of Tartu and the main collaboration was done at the Institute of Physics, Institute of Chemistry and Haine Paelavabrik OÜ.

1. INTRODUCTION

1.1. Ionic liquids

An ionic liquid (IL) is a salt in which the ions are poorly coordinated, which results in these solvents being liquid at room temperature (RTIL) or below some arbitrary temperature, such as 100 °C [8]. The history of ionic liquids dates back to 1914, when Latvian scientist P. Walden revealed the first ionic liquid – ethylammonium nitrate with a melting point at 12 ^{o}C [9]. The widespread use of these molten salts began 22 years ago, starting with the discovery of a new class of air and water stable ionic liquids by Wilkes in 1992 [10]. Worldwide intense research activity in the field of ionic liquids is presently going on. Ionic liquids are currently widely used in synthesis [11] and catalysis [12], because of their remarkable physic-chemical properties such as negligible vapor pressure, nonflammability and a wide liquid-state temperature range [13;14]. Due to the non-volatility, ionic liquids have advantages in extreme conditions, where ordinary organic compounds evaporate (in high vacuum up to 10^{-9}) [15]. The most applicable field of using ionic liquids is electrochemistry, because ionic liquids have high ionic conductivity and a wide electrochemical window (up to 6V) [16]. Many groups of ionic liquids are thermally stable at temperatures higher than 570 K as well as being air and water stable [8;11].

Ionic liquids are more viscous than ordinary molecular solvents. At room temperature their viscosity varies from 10 mPa·s to more than 500 mPa·s [8;11]. In addition to temperature, viscosity depends on the structure of the cation and the anion and of the impurities contained in the material. They are ideal reaction mediums for the chemical and biochemical reactions, because they are capable of dissolving polar and non-polar, organic and inorganic, and polymeric compounds. With all these properties, ionic liquids can replace volatile organic solvents in several chemical reactions [17;18], especially in organometallic catalysis processes, in relation to their capability to be recycled and recovered.

The attractive advantage of ionic liquids is the possibility to combine different anions and cations during the synthesis which will change their properties significantly [19]. The number of anion/cation combination is undefined, it is mentioned that different structure combinations in ionic liquids have approximately 10^{18} possibilities [10].

Most applicable ionic liquids are based on organic bulky and asymmetric imidazolium or quaternary ammonium cations (Figure 1). Anions are mainly weak ligands and poorly coordinated inorganic or organic moiety (Figure 2). Ionic liquids containing BF_4^- are widely used in many applications [14]. Properties such as an inertness to moisture and oxygen, poor coordination ability, and a weak ligand makes BF_4^- a significant anion to ionic liquid [12].

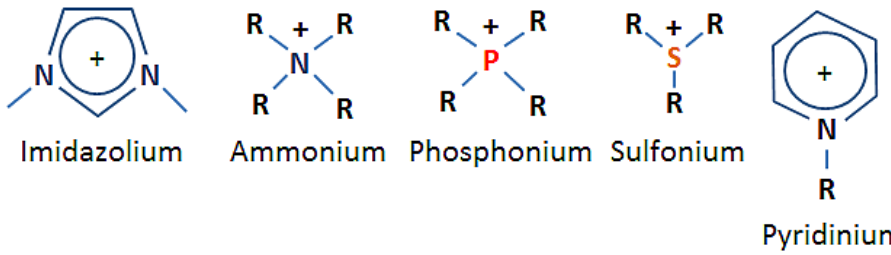


Figure 1. Commonly used cations to synthesize ionic liquids.

The properties of an ionic liquid depend largely on the choice of anion cation combination. The oxidation properties of ionic liquids depend on the chain lengths of cations. Oxidation ability is lower for cations with small chains. To modify the physical properties of the ionic liquids, special functionalized ionic liquids are synthesized (also called task specific ionic liquids). In such case, cation or anion is covalently modified by a functional group.

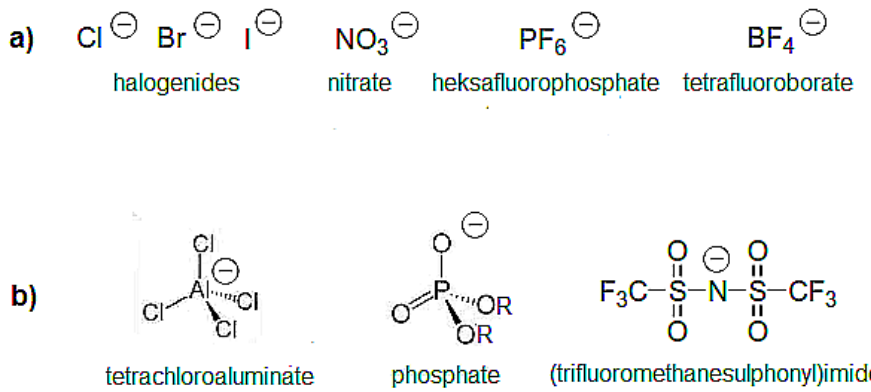


Figure 2. Anions to synthesize ionic liquids, a) commonly used b) more specific use.

1.2. Imidazolium based ionic liquids

Imidazolium based ionic liquids have been at the focus of a rapidly growing number of studies in the last decade [11]. Among the other cations, the ionic liquids with imidazolium cations exhibit higher ionic conductivities and lower viscosities, which are important in many applications [20]. For practical use, researchers have been designed ionic liquids cations and anions to control their physical properties. The transform of the coordination of alkyl chains on the imidazolium ring cations and the selection of large anion species have been the

main objectives to control imidazolium based ionic liquid physical properties. However, increasing the chain lengths of the imidazolium ring, melting point of ionic liquid also increases [21].

Many ionic liquids are largely structured ions and ions pairs. Imidazolium based ionic liquids are also known as supermolecular ion structures or aggregates (Figure 3) [22]. In C2 position of the ring proton (C2H) located between two electronegative nitrogen atoms, the acidic character determines the extended hydrogen bonded networks of liquid phases. It has been showed that there exists a very strong interaction between the imidazolium hydrogen atom and the two nitrogen atoms next to it [23;24]. It is proposed that the properties of imidazolium based ionic liquids strongly depends on the length of the alkyl chain on the imidazolium ring. For a longer carbon-chain, ionic liquid structure is maintained as a smectic phase of liquid crystals [24]. Imidazolium based ionic liquids are structured on a nanometer-scale. In [24;25] the computer simulation illustrates the model how pure ionic liquids of the 1-alkyl-3-methylimidazoliums show structuring in their liquid phases analogous to microphase separation between polar and nonpolar domains. It has been showed that for ethylmethylimidazolium ionic liquids the polar domain has structured. A tridimensional network of ionic channels is showed that the nonpolar domain is arranged as a dispersed microphase and as a continuous one for longer side-chains (hexyl, octyl or decyl). The butyl side-chain would indicate the outset of the transition from one type of structure to the other. Thus ionic liquids can contain both ionic and molecular state in solutes [24;25].

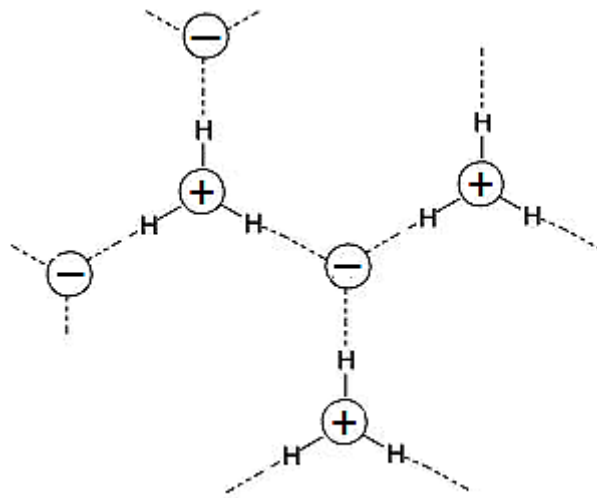


Figure 3. Two dimensional model of the supermolecular structure of 1–3 dialkylimidazolium based ionic liquids. Hydrogen bond are formed between imidazolium cation (+) and anion (-) [22].

Ionic liquid interaction with other materials can influence their properties significantly. Nevertheless, their advantageous liquid state turns out to be an impediment for applications in devices, which need solid state shaping. Next sections provide an overview of how to solve these problems.

2. IONOGELS

It is well known that ionic liquids have high ionic conductivity, wide electrochemical potential window and therefore have been used as electrolytes in fuel cells, solar cells, and lithium – ion batteries, also in optics, catalysis and modification of materials. Often there is difficult to use liquid substances in these applications, so there is frequently a need for immobilizing ionic liquids on solid matrices which are consistent with ionic liquids liquid-like dynamics, to avoid leakages and to miniaturize impediments. Obtained materials are called ionogels. By on possible definition, ionogels are hybrid materials that consist of an ionic liquid and a solid 3D network (gel) intermingled at nanometer scale and have ionic liquid properties without leaking [7]. There are mainly two classes of ionogels: organic ionogels – ionic liquid is immobilized, into organic solid network; inorganic ionogels – ionic liquid is immobilized into inorganic solid network.

2.1. Organic ionogels

In organic ionogels the solid network is usually achieved in situ. Gels can be procured by carrying out polymerization in the ionic liquid, or by swelling of polymers. Most of organic ionogels are also known as physical ionogels, except polymerized ionic liquids [7;24].

2.2. Inorganic ionogels

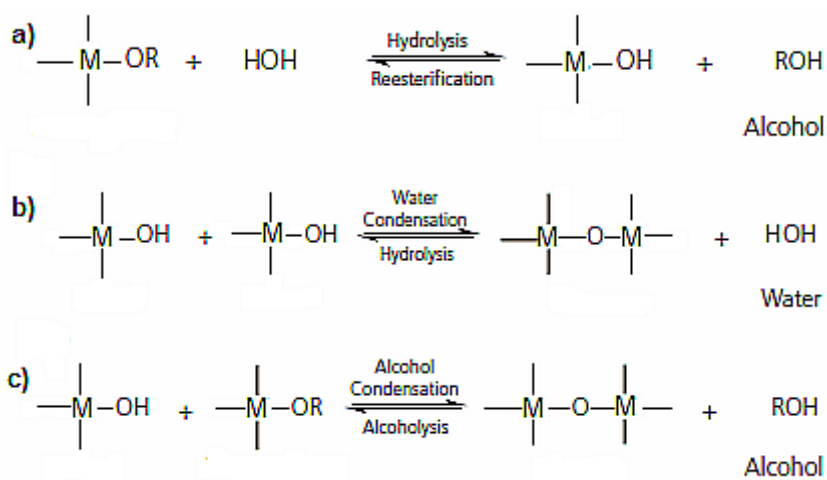
Inorganic ionogels are typically synthesized through sol-gel chemistry or impregnation ionic liquids in oxides, metals or carbon particles. Most of inorganic ionogels are also known as chemical ionogels, covalent bonds between the liquid base and solid matrix can be obtained [7;24]. (section 2.3; paper 3).

2.3. Sol-gel method for inorganic imidazolium based ionogels

Sol-gel is commonly used “wet chemistry” method to synthesize principally inorganic oxide materials. Compared to the classical methods - most widely used synthetic technique for bulk oxides - ceramic and glass technology, sol-gel method is much cheaper, because the temperature required for obtaining products can be remarkably lower. Thereby giving the certain shape and size of the obtained material is flexible due to the rheological properties of the precursor gels. In fact, there are mainly two methods of sol-gel chemistry – aqueous and nonaqueous. The aqueous sol-gel process can be defined as the transforamtion of a precursor solution into an inorganic solid via inorganic polymerization reactions induced by water. In nonaqueous sol-gel chemistry the transformation of the precursor takes place in an organic solvent under

exclusion of water. Comparing to aqueous sol-gel chemistry, potential precursors are more than nonaqueous sol-gel, metal acetates and metal acetylacetonates are included in addition to inorganic metal salts and metal alkoxides [26].

The sol-gel chemistry has been extensively studied since the early 1980s. [27]. Many authors nowadays agree that processes start with the formation of densely distributed partially crystalline metal-oxo nanoparticles, which are spatially stabilized by a shell of alkoxy groups. In later stages, the particles can form different secondary structures like clusters, gel networks, linear chains etc [28]. Chemical processes play a relevant role in controlling the sol-gel process. Metal alkoxides are compounds which have an organic moiety attached to a metal or metalloid atom through oxygen atom [26;29]. Hydrolysis and condensation processes depends mainly on the electronegativity of the alkoxy groups and therefore it shows the chemical reactivity of metal alkoxides, properties like electronegativity, ability to increase the coordination number, the monomeric or oligomeric structure of the metal alkoxides, and the steric hindrance of the alkoxy group [26;28;29]. The amount of added water in the hydrolysis step determines, whether the alkoxides are completely hydrolysed or pre–polymerized and which oligomeric intermediate species are formed plays a key role in sol-gel chemistry [5;26]. Widespread knowledge of sol gel chemistry is described in Scheme 1. The overall process of hydrolysis is summarized in Scheme 1 a). Two partially hydrolyzed molecules can link together in alcohol condensation (alcoholysis) reaction (Scheme 1 b). Therefore the equimolar amount of water is not necessary for the completion of sol-gel process.



Scheme 1. a) Hydrolysis of metal alkoxide in sol-gel processes; b), c) - condensation reactions between two partially hydrolyzed molecules

On current opportunities of sol-gel method, it is efficient and effective to extend the knowledge to new class of hybrid materials – ionogels, thereby including the clarification of their cognitive and practical applications.

Most works involving sol-gel processing in ionic liquids are performed in imidazolium salts. Ionogel prepared by sol-gel method can be defined as a solid interconnected matrix distributed throughout by liquid phase. Using classical sol-gel method, gel is used as a precursor obtaining solid porous materials (xerogels, aerogels, or ceramics after heating). Gel itself is difficult to keep stable in humid air, for the excision of solvents and water. The use of ionic liquids, which have negligible vapour pressure, permits one to regard the gel (also called aquogel or alcogel) itself as a material. Sol-gel synthesized ionogels combine the properties of the two systems (oxide and ionic liquid) intermingled at nanometer scale. In other words, by combination of ionic liquid and metal alkoxides it is possible to create new nano-fine metal oxide porous cross-linked systems which have practical applications in various fields (e. g. solid electrolyte membranes, selective absorbing material, optical components, and catalyst carrier - section 3) [6]. In creation of such materials ionic liquids are used as nano-pore templates inside a host matrix. This technique relies on the use of an ionic liquid as both the solvent and the structure-directing agent due to their nanostructural organization. A specific nanostructure of ionic liquids is likely induced at the surface of nanoparticles, which should influence aggregation processes.

3. APPLICATIONS OF IONOGELS

It has been shown that ionogels have similar conductivity as the source ionic liquid used [30;31]. Ionic conductivity of the ionogels follows closely the Arrhenius plot when the temperature and viscosity are changing [24]. Viscosity is largely influenced by the amount of water inside the ionic liquid. For example, increasing the amount of water in [BMIM] [BF_4] by 2% of its mass decreases the viscosity of the ionic liquid by 50% [11;24]. This dependency only occurs when the ionic liquid is water soluble. As sol-gel method involves hydrolysis of alkoxide and/or condensation of alcohol, and amount of water is needed. All ionic liquids contain some amount of water, which must be taken into account in the synthesis of ionogels. One characteristic trait of ionogels is an opportunity to functionalize them, disperging functional molecules, metal complexes, or nanoparticles in ionic liquid. Those qualities are important in applications as new hybrid material has versatile and mutable features.

3.1. Synthesis of nanoparticles

A novel concept in the process of nanoparticle preparation is synthesizing them in ionic liquid environment which guarantees homogeneous dispersion of nanoparticles during the process.

Several papers have demonstrated that producing nanoparticles in ionic liquid is technologically promising and fast-growing field as ionic liquids are effective in disperging produced particles as well as being the medium for the synthesis [32;33;34]. Also, it is possible to obtain gels with narrow size distribution – nanodispersions – pulverizing macroscopical substance in ionic liquids [35]. Promising feature of ionic liquids in ionogels is an opportunity to use their influence on the size and structure of the nanoparticles combining different cations and anions of ionic liquid [36]. Ionic liquids act as supra-molecular solvents, therefore developed and well-defined nanoparticles can take place within them (Figure 4; 5).

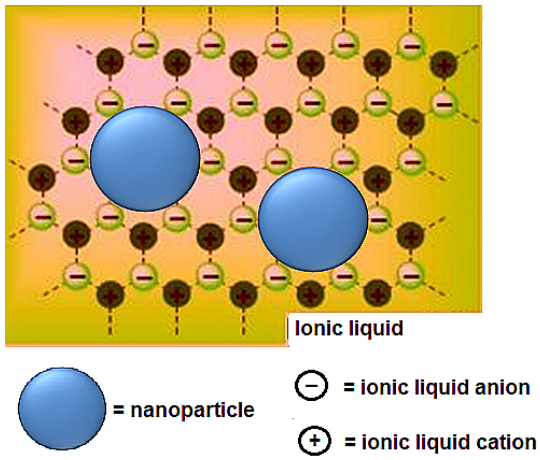


Figure 4. Some ionic liquids generate a protective layer which avoids the use of different stabilizing agent like coordinating ligands or fasten polymers. Therefore ionic liquids prevents nanoparicles from aggregation and agglomeration processes [37].

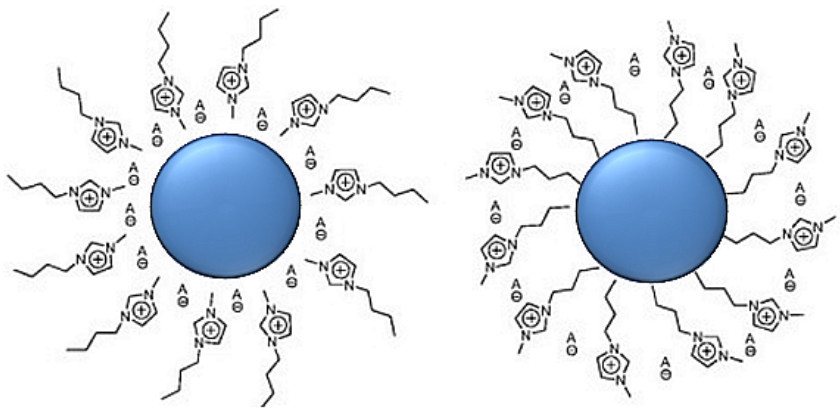


Figure 5. Nanoparticle stabilization model in ionic liquids. Surface charged particles of the left, neutral particles of the right [36].

3.2. Ionogels as electrolyte materials

Ionogels, which incorporate both chemical and physical qualities of the ionic liquid as well as size and shape flexibility of matrix, create novel effective ways to apply those systems to develop conductive materials for electrochemical appliances (batteries, fuel elements, photogalvanic cells, etc). Solid electrolytes were prepared using emulsion of [BMIM][NTf_2], $TiCl_4$, methanoic acid, and methanol which was sonicated with ultrasound and dried at 80 ^oC. Procured solid electrolyte materials showed high conductivity (10^{-2} S/cm at 275 ^oC) due

to the formation of nanostructural canals of ionic liquid. Homogeneous distribution of ionic liquid in material was not achieved: it formed pores or canals depending on the concentration of ionic liquid [38]. Recently, a novel ionogel based on carbon nanotubes (bucky gel) was developed [39]. Addition of carbon nanotubes (CNTs) resulted in both ionic and electron conductivity of material being 0,18 mS/cm. It has been shown that SiO_2 nanoparticles start to aggregate in IL – [EMIM][NTf_2] – which results in a network of SiO_2 particles in ionic liquid. High performance electrolytes have been obtained adding CNTs into the process of gelation. Ionogels have been used to develop novel colour-sensitive quasi solar cells. Colour-sensitive solar cells depend upon accumulation of thin photosensitive paint onto conductive surface, for example, porous layer of titanium oxide nanoparticles. Electrolytes of this cell were prepared using sol-gel method based on silicon and several surface-active mixtures along with ionic liquid based on imidazolium iodide [31]. It was shown in the work that dialkylimidazolium cation formed a covalent bond with trimetoxysilyl group during sol-gel process. Applying processes of sol-gel chemistry and heating the materials obtained at 200 ^{o}C resulted in a solid transparent electrolyte material for colour-sensitive (Graetzel type) solar cells. Ionogels obtained using sol-gel method have been discussed in the paper published in 2013 [40], where it was shown that prepared ionogels can potentially be used as solid electrolytes in high-temperature electrochemical appliances because developed materials are thermally stable up to 450 ^{o}C and possess high ionic conductivity at room temperature (3,1 mS/cm). Ionogels were prepared using [BMIM][BF_4] and tetraethoxysilane. Using this method, the obtained ionogel had high ionic liquid content (97% of mass), and stayed stable for several months. High content of ionic liquid without leakage was explained by hydrogen bonding between BF_4^- anion from ionic liquid and hydroxy groups on the silicon surface. The possibility of using highly conductive transparent ionogels (10^{-2} S/cm at 25 ^{o}C) synthesized from tetraethoxysilane and [EMIM][NTf_2] as electrolytes in electrochromatic appliances has been investigated as well [41;42]. Development of solid and flexible electrolytes is highly important for supercapacitor applications.

3.3. Ionogels in optics

Ionic liquids are attractive optical solvents not only because of the stability and non-existent vapour pressure but also because of their transparency at almost full range of visible and near-infrared spectrum. Usage of ionic liquids as optical materials is limited due to the liquid state. Ionic environment of ionic liquids enables to form gels with several ion-coordinated compounds (lanthanides, salts, various complexes. The ionogels containing lanthanide complexes have been shown to have extremely high photostability. Hybrid material with novel properties of luminescence and ionic conductivity has been obtained disperging europium complex in ionic liquid and binding SiO_2 matrix of ionic liquid [43].

4. TEXTILES – IN A FIELD OF MATERIALS SCIENCE

4.1. Textiles for daily use

Textiles have been for a long time and still are one of the most important fields in research. Textile materials have played a central role in history. Natural fibers, such as cotton, flax, hemp and silk have been used for centuries, and the significant efforts have been made to improve the durability and flexibility of these fibers. Textile materials offer a several advantages that make them almost irreplaceable for clothes or for technical textiles. Textile can be perform in many different ways, they can be fabricated to be flexible as well as inflexible for several times, they can show a certain breathable for air, vapour or liquids. Textiles combine great physical and chemical stability (especially tensile strength). Fabrics can be produced with large quantity while being at relatively light in weight. Taking into account of these properties textile approaches offer solutions advantageous in price and performance [44].

4.2. Functionalization of textiles

Improving textile main properties and creating new materials with advantageous properties are the major grounds for the modification and functionalization of textiles. Several methods can be used to functionalize textiles. Most common of these are coatings and finishing, plasma treatment, lamination, hot melting, UV curing and sol-gel method. Textile coating typically comprises two parts: binder for durability and additives for functionality. The choice of method depends on the characteristics of what we want to achieve the product obtained (Figure 6).

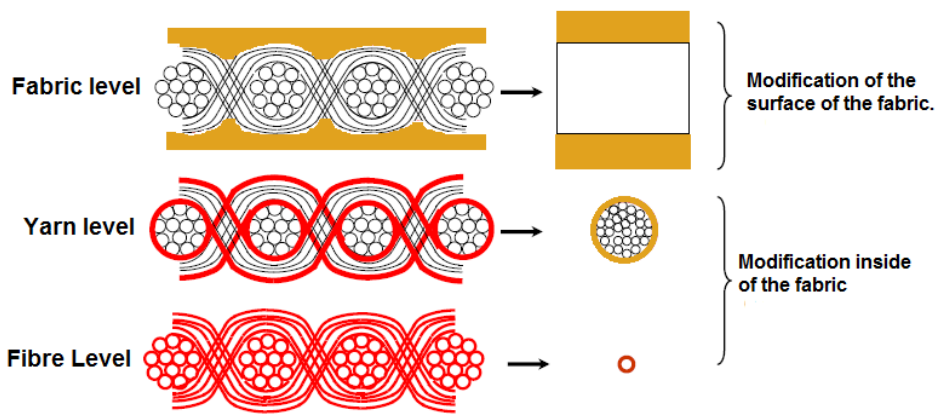


Figure 6. Potential levels of coating fabrics [45].

Functionalization of textiles is carried out with the view of obtaining stability against mechanical, chemical, or thermal destruction; to improve repellency properties against water, oil and soil; to modify light absorption and emission properties from the UV up to the IR region, to increase electric conductivity for electromagnetic properties, and to connect homogeneously active species (silver nanoparticles) for antibacterial use. The most promising method to improve aforementioned properties is a sol-gel method [46]. Overview of this method to show textile coatings is given in next section.

4.3. Sol-gel coatings

The sol-gel technique offers various possibilities for creating new surface coatings with different functional properties. Sol-gel technology gives us a possibility to design surface properties by combining specific properties of different chemical compounds in a single composite material. The application of sols can be accomplished with techniques widely used in the textiles industry at the same time [44]. The coating of textiles with chemically or physically modified sols enables the alteration of their different properties (Figure 7).

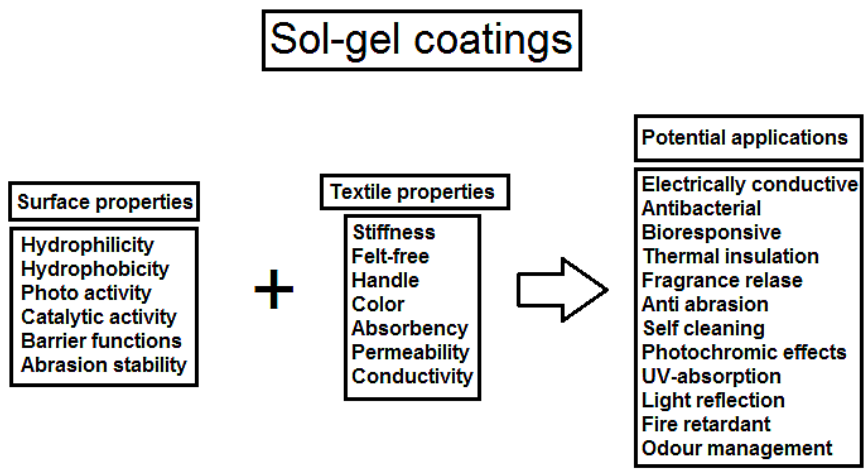
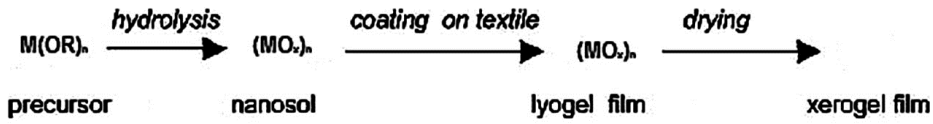


Figure 7. Sol gel coatings for textile: potentials and applications.

The functionalization of textiles by coating with sol-gel method based on modified silica is the most frequently used method [47;48] (Scheme 2.).



Scheme 2. Functionalization scheme of modifying textiles by silicon alkoxide [47].

In described work it has been shown that there are four basic steps for treating textiles with silica alkoxides. This scheme is easily expandable to include other metal alkoxides. When treating textile substrates with a solution (sol), nanoparticles condensate and aggregate into a three-dimensional network due to their quite large surface to volume ratio. Then they form a lyogel layer containing solvent on the textile surface. After that when this lyogel is dried or heated to remove solvent from the coating, a xerogel film is obtained on the textile surface [47].

Using different metal alkoxides as a precursor, cracking is characteristic in sol-gel processes during curing of the material. Crack formation and development in sol-gel films has been studied in cases where the film is firmly attached to substrate [49;50;51;52]. In addition to curing conditions (speed and temperature), material thickness is determinative as well. It has been shown that for titania films made by titania-alkoxide cracks are inevitable when the thickness exceeds 1 μm [53]. The matter of the stress and consequently crack formation during the gelation can be explained by the formation of pores within the gel that are filled with the solvent. During the continuing evaporation of the solvent and the further condensation processes of the sol-gel chemistry, these pores collapse. Increase of tension is the result. (see Figure 8) [44;54;55]. In thin titania films (<100 nm of thickness) there is an interaction between sol and gel, and in such case the situation can`t be described as cracking of a secluded film [44].

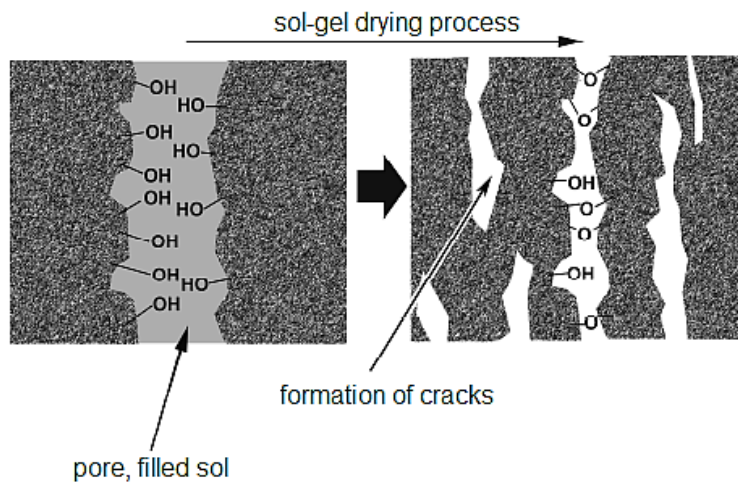


Figure 8. Drying process of titania films made using sol-gel method [44; 54;55].

4.4. Sol-gel method for chemical modification of textile fibers

Chemical modification or chemical finishing of textile fibers using sol-gel method consists of treating textiles with sol, and drying and curing fibers under the appropriate conditions. Different textile fibers have different functional reactive groups. (e.g. OH-cotton, wool, polyester; CN-polyacrolynitrile; NH_2-polyamide). Functional group prevents collapse of the pores and formation of the cracks. Using metal alkoxides as precursor materials, "M"OH groups of precursors can react with the fiber surface forming hydrogen bonds as well as covalent bonds. (Figure 9).

Obtained organic-inorganic materials have rather different properties of the starting materials, bu this dual system does not contribute significantly to the polymer and hardness of the ceramics. As it was mentioned in the last section, thickness of the material is determinative to avoid cracks. Covalently bonded thin oxide films on the surface of the appropriate functional group textile prevent collapse of the pores and formation of the cracks (Figure 10).

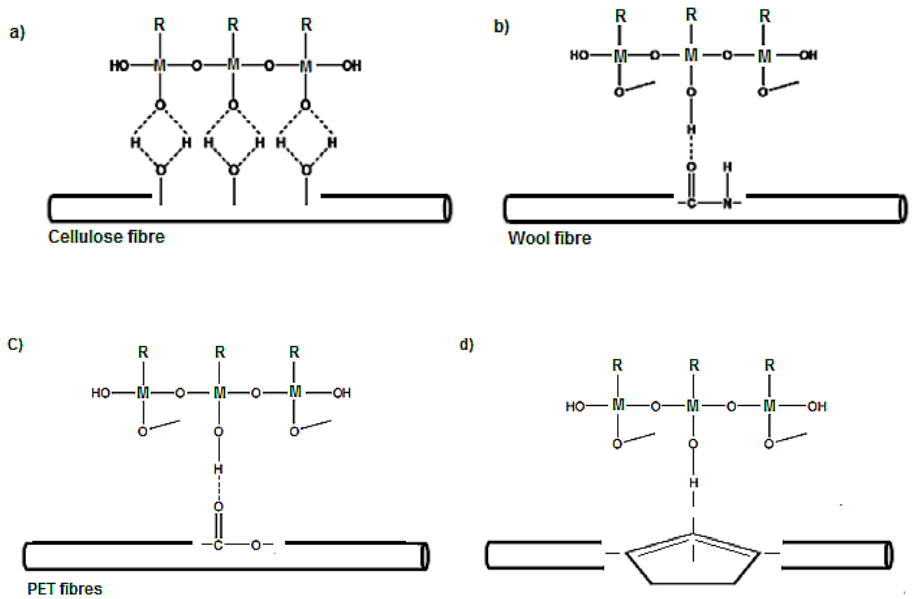


Figure 9. Functinalization of different textile fibers using metal alkoxides as precursor materials. Hydrogen and covalent bonds form. a) cellulose; b) Wool; c) and d) different functionalization opportunities of polyethylene terephthalate fibres [56].

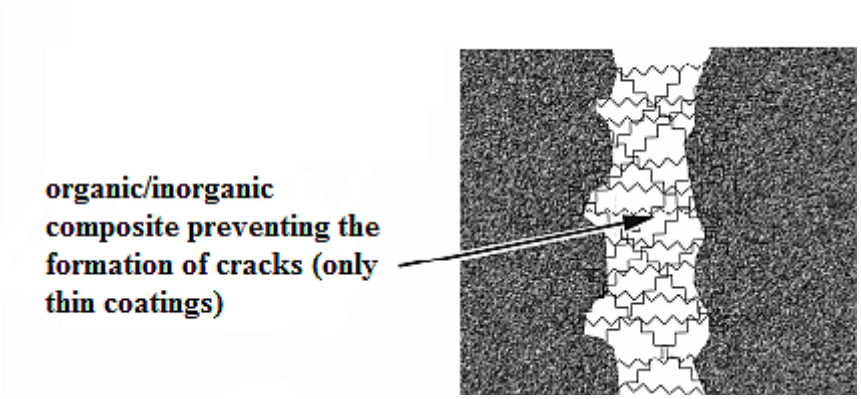


Figure 10. Chemically bonded metal oxide films on the surface. Functional group textile prevent collapse of the pores and formation of the cracks [44].

Due to the extremely thin polymer film on the surface of the textile, it does not cause any significant influence to the physical properties of the textiles such as tensile strength, softness and elasticity [56]. Moreover, due to the extremely rigid ceramics (oxides), modified textile shows tendency towards cracking or crumbling under mechanical influence (Figure 11). To overcome these problems and to improve textile properties using thicker coatings, ionogel is one of the promising opportunity (next section).

Figure 11. Single cotton fiber modified using titania-sol. Non-stable coating and plenty of cracks on the surface are showed.

4.5. Ionogel coatings

Our work focuses on combining metal alkoxide and ionic liquid for preparation of textile coating with different functionality. Ionic liquid covalently bonded to micro– and nanoscale network in metal alkoxide improves many textile properties. Ionic liquids have many promising properties for functionalization of textiles, but their advantageous liquid state turns out to be an impediment for applications of textiles. Obtaining ionic liquid properties in solid matrices could be the solution. Below, the latest results of ionogel coatings are described.

A photoresponsive gel used for textile coatings has been described to result in a hybrid material which is a photoresposive ionogel [57]. A photo-initiator DMPA and a trihexyltetradecylphosphonium dicyanoamide ($[P_{6,6,6,14}][dca]$) ionogel was used. A fabric comprising a photo-responsive polymer polymerized within an ionic liquid matrix so as to form a photoresponsive ionogel, where the ionogel is crosslinked or covalently coupled to a textile (woven or other formed textile based products) component of the fabric. As body temperature increases due to direct sunlight these materials become more liquid in form and heat transfer properties are enhanced, enabling heat to be more effectively transferred to internal layers, which increases the cooling effect of the textile. On the other hand, when external temperatures drop due to lack of sunlight these materials solidify, and heat retention within the material is enhanced reducing the loss of body heat to the external environment.

Another work describes using ionogels as electronic textiles and mainly targets applications based on physiological parameters [58]. Ionogel poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid - (PEDOT:PSS) is used as a flexible biosensor that can therefore be incorporated into daily fabrics allowing for the analysis of real time measurements of the target biomolecules. It is reported that PEDOT:PSS is capable of sensing glucose in a neutral pH buffer solution [59].

Inorganic ionogels are also used as bridges in order to expand the properties of some other materials (e.g. carbon nanotubes). Using ionogels carbon nanotube transistors stretches further than previous devices. Such systems can be mounted on a textile and can withstand twisting and stretching, and still turn on and off [60]. In the next section the system of carbon nanotubes and ionic liquids is described.

4.6. Carbon-nanotube-ionic liquid gels

Carbon nanotubes (CNTs) have a unique spectrum of extraordinary mechanical, electrical, and thermal properties that guarantee them numerous potential applications in material science [61], particularly in reinforcing different composites. Main challenges for integration of these exceptional carbon fibers in various media include uniform dispersion, preferential alignment, and mass-production of high-purity material at low cost [62]. It is well-known fact that CNTs are hard to process due to their tendency to form agglomerates. To

overcome this problem different approaches were suggested in literature to decrease the nanotube agglomeration, such as ultrasonication, high shear mixing, and methods, which are aimed to change the surface chemistry of the tubes either covalently (functionalization) or non-covalently (adsorption) [62].

A decade ago, an alternative solution to the problem of low dispersibility of CNT was found. In 2003 Fukushima et al. reported that imidazolium based ionic liquids can separate the CNTs agglomerates [63]. Ionic liquids consist solely of ions and are fluid at room temperature. As it was mentioned before, ionic liquids have been in the focus of many researches during the last 20 years because of their remarkable physicochemical properties. In this context materials based on CNTs and ionic liquids, also called bucky gels, have attracted much attention due to synergetic combination of properties of both components. CNT-ionic liquid mixtures have been intensively studied in the field of catalysis, in electrochemistry and in composite materials with polymer matrices [64]. However, polymer materials have some disadvantages related to poor thermal and chemical stability. CNTs and ionic liquid incorporation into inorganic matrices by sol-gel process definitely have some advantages over polymeric matrices. However, there have not been many studies in this field [65].

5. RESULTS

5.1. Aims of the study:

Author's research is focused on using ionic liquids and sol-gel technology for the creation of new functional nano-composites by combining modern theories, methods, and ideas. The works dealing with ionic liquids are of exponentially growing interest, which was described in the previous sections. The aim of this study was to combine different imidazolium based ionic liquids with different metal alkoxides to produce novel homogeneously dispersed materials by giving them suitable shape and size using aqueous sol-gel reaction. However, it was revealed that at the first sight some safe and green ionic liquids may be useless or even dangerous in described composites due to their changes in the structure at ambient conditions (Paper 1). To expand the understanding of the formation processes of sol-gel chemistry, different shape and sized materials were obtained (Paper 2). Ionic liquid miscibility with metal alkoxide plays an important role in the production of homogeneous composite. Also, a problem to be solved in this work comes from the fact that it is hard to dissolve polar ionic liquids in non-polar metal alkoxides (Paper 3). Considering the applications of the new hybrid ionogel, functionalization of cotton fibers has been stated as the main goal of the study (Paper 4).

All the papers are synergistically related and one complements the other. Author has been a corresponding author of all the published papers and has been dealing with problems to overcome interconnected barriers of theoretical and experimental work dealing with novel hybrid materials. The published papers are closely combined in order to coordinate the aim of the study.'

5.2. Equipment and measurements

Infrared (IR) spectra for two component crystal structures and different shape and sized hybrid materials were recorded on Spectrum BXII FTIR spectrophotometer (Perkin Elmer). The spectra of high resolution mass spectrometry (HRMS) for detecting ionic liquid components in cluster crystals were measured on a Electron LTQ Orbitrap ESI spectrometer (Thermo scientific), the sample was dissolved in acetonitrile (ACN). Crystallographic studies of the crystal product were carried out using SMART Apex-II multipurpose (single crystal and powder) X-ray diffractometer (Bruker) operating at room temperature with MoKa radiation (l¼0.71073 A˚). The single crystal data was collected up to 2yr421 in the view of possible disorder in the crystal. The structure was resolved using direct methods, and all atomic positions were refined by full-matrix anisotropic approximation. Final discrepancy factors were R1¼0.0919 and wR2¼0.2253 for the 252 observed reflections (I42sigma(I)). The powder data were collected for a multicrystal sample in a rotation mode in a sealed capillary. The data collection, reduction, and integration were carried

out using Bruker Apex-II program package. The phase identification was performed using the Bruker EVA powder data evaluation program. All the optical characterizations were carried out using a BX 51 optical microscope (Olympus). The scanning electron microscopes (SEM) were used to visualize all the results in micro and nano level. The imaging of two component crystal structures, gel and oxide microrols, homogeneous and poroeus ionic-liquid-alkoxide composites, hybrid carbon-nanotube-ionic-liquid-alkoxide systems, and functionalized textile threads was performed on a Vega microscope at 10 kV (Tescan). Carbon tape and fine polished silicon substrates were used for sample preparation. Energy-dispersive X-ray spectroscopy (EDX) analyses for element analysis were performed on a Helios NanoLab 600 SEM (FEI). The results of thermal analysis were measured for the knowledge of the de-composition of cluster crystal structures and hybrid ionic liquid – oxide materials. Thermogravimetric (TGA) measurements were performed on a TGA analyser-Thermal analyzer SetSys Ev 1750 (Setaram Instrumentation) with DSC Plate rod in Pt crucible 100 mL, at heating rate 10 1C/min up to 600 1C in Ar flow 60 ml/min. Differential scanning calorimetry (DSC) was carried out on a DSC 7 analyzer (Perkin-Elmer) with heating and cooling rates 10 1C/min. Nitrogen was used as the furnace purge gas. Temperature and heat flow calibrations were done with indium and tin standards. Photodissociation of ionic liquid $EMIMBF_4$ vapors was performed at an undulator beamline I3 of the MAX-III synchrotron radiation facility (Lund, Sweden) **(**S. Urpelainen, 2009**)**. The beamline is equipped with a normal incidence monochromator. A MgF_2/Al coated grating was used in the monochromator and the higher harmonics of the undulator radiation were blocked by a LiF crystal. This limits the highest energy dependent TOFMS spectra to about 10.5 eV. The time of flight mass spectra (TOFMS) and partial ion yield (PIY) spectra were recorded using a Wiley-McLaren type ion time-of-flight (TOF) spectrometer with a 320 mm drift tube and a 77 mm diameter Hamamatsu microchannel plate detector. ^{1}H- and ^{13}C-NMR spectra for characterizing synthesized ionic liquid MTICl were recorded at ambient temperature on a Avance II 200 spectrometer (Bruker), using DMSO-d_6 as a solvent. The ^{1}H-NMR spectra were measured at 200 MHz and the ^{13}C-NMR spectra at 50 MHz. The chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. 29Si NMR spectrum for chemical Si bonds of solid ionic-liquid-alkoxide sample was recorded on Bruker AVANCE-II spectrometer at 8.5T magnetic field, at resonance frequency of 71.45 MHz using a home built magic angle spinning (MAS) probe for 10 mm zirconia rotors.

5.3. The stability of ionic liquids (Paper I)

During recent years, investigations on stability of ionic liquids in combination with different solvents have been increasing and this may lead to number of investigation of experimental design and utilization of these chemicals.

Although ionic liquids have negligible vapour pressure, in some cases vaporization is still occurring. It has been shown that some ionic liquids can even be distilled in a vacuum with little thermal degradation [66]. Moreover, ionic liquids based on BF_4 and PF_6 anions, are hydrolysed already at room temperature [67;68]. In addition, photodissociation of [EMIm]BF_4 ionic liquid vapours following excitation with light in the vacuum. Ultraviolet region has been studied at different temperatures [69].

The regular complex crystals of Na_2SiF_6 have been obtained in the aqueous solutions of different methylalkylimidazolium (ethyl-, butyl- and decyl-) tetrafluoroborate ionic liquids. It has been demonstrated that sodium hexafluorosilicate crystalline compounds with good regularity and narrow size distribution containing dialkyl imidazolium ions between the nano hexagonal crystalline clusters interconnected to each other to a whole hexagonal aggregate can be obtained in large quantities. This characteristic phenomenon of crystallization in ionic liquid media is reported for the first time. The mechanism of formation of various [RMIm]BF_4-Na_2SiF_6 microcrystalline morphologies and the influence of temperature on growth kinetics were discussed. To improve the discussion, different measurements were carried out. Crystallographic studies of the product were carried out by X-ray diffractometer (XRD), characterization by scanning electron microscopy (SEM) and optical microscopy; also infrared spectra (IR) were recorded. Thermal analyses were performed by differential scanning calorimetry-thermogravimetric analyser.

Novelty of this work is exceedingly high as according to our knowledge this characteristic phenomenon of crystallization in ionic liquids containing BF_4^- ions is reported for the first time. Described cluster structures can have several potential applications in different fields due to their comb-clustered complex structure. These two-component systems can have variable refractive index. The presence of conductive ionic liquid between the crystalline layers makes them also attractive.

According to experimental results, the main results and conclusions are:

- The thermal and chemical decompositions of tetrafluoroborate-based ionic liquids in aqueous solutions were evaluated. Differential scanning calorimetry (DSC) measurements were carried out with crystal structures, which were synthesized from three different precursors: [EMIm]BF_4, [BMIm]BF_4 and [DMIm]BF_4. It is demonstrated that all these crystals have similar thermograms. Decomposition peaks in the figure correspond to the ionic liquid (Figure 12).

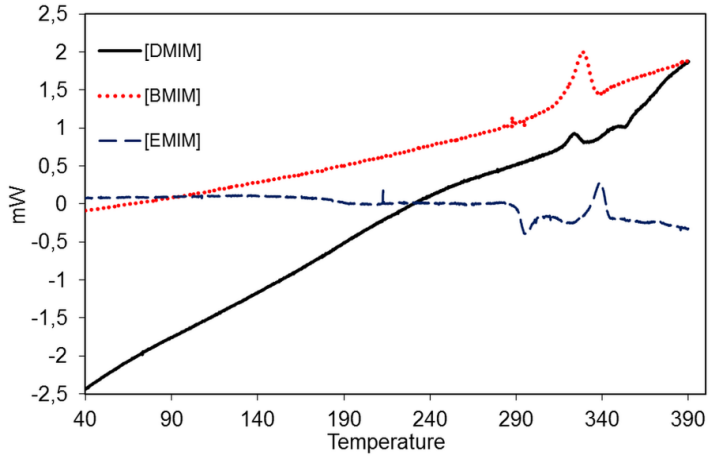


Figure 12. Differential scanning calorimetry of different [RMIm]BF_4–Na[SiF_6] crystals. The decomposition peaks at ~300-340 C^o are characteristic to RMIm]BF_4 type ionic liquids [70].

- High resolution mass spectrometry (HRMS) analysis of positive ions of crystals gave only one signal at 111.09088 which corresponds to the calculated value for 1-ethyl-3-methylimidazolium ring ion mass 111.09167.
- At different temperatures (even at room temperature), our studies showed that tetrafluoroborate anions hydrolyzed to [BF_3OH]. Moreover, hydrolysis increased rapidly, rising the ionic liquid/water solution temperature.
- The coexistence of two compounds in our crystals presumes the quite regular structure of material. For better view into the crystal series of SEM measurements were carried out. Mechanically cleaved crystal and hypothetical scheme of two compound cluster system was represented. Na_2SiF_6-ionic liquid cluster system can be described by an electrostatic interaction model, where negatively charged fluorine atoms are located on the surface of single sodium hexafluorosilicate clusters and they interact with positively charged ionic liquid imidazolium ions (Figure 13).

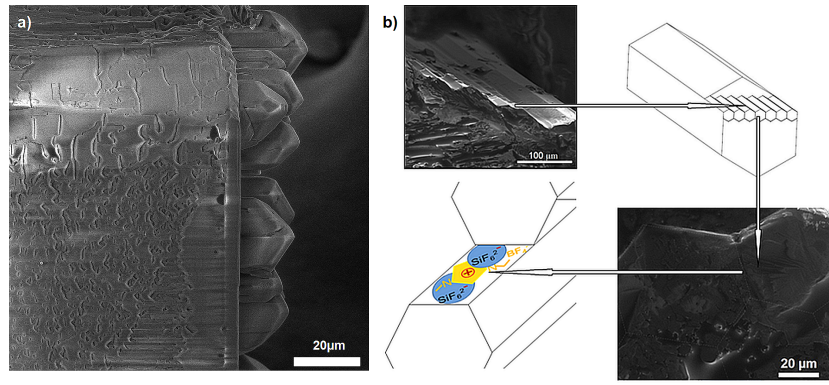


Figure 13. a) The cross section of the crystal, b) SEM images of mechanically cleaved crystal and a hypothetical structure of two compound cluster systems [71].

- The size of the cluster crystals varies depending on the concentration of ionic liquid-aqueous solution. The impact of concentration and temperature on the cluster crystal approximate length in one dimension is presented. It was demonstrated on certain concentration interval in which crystals can be obtained.
- Formation of IL-sodium hexafluorosilicate structures is not completely understood and the crystallization process of inorganic crystals needs further investigation. Furthermore, tube-like crystals were obtained, where the body of the crystal is formed of $Na[SiF_6]$, and $[RMIm]BF_4$ type ionic liquid covers the surface of the crystals Mechanically cleaved structures are showed in Figure 14, but it should be taken into account that the results primarily show cognitive values.

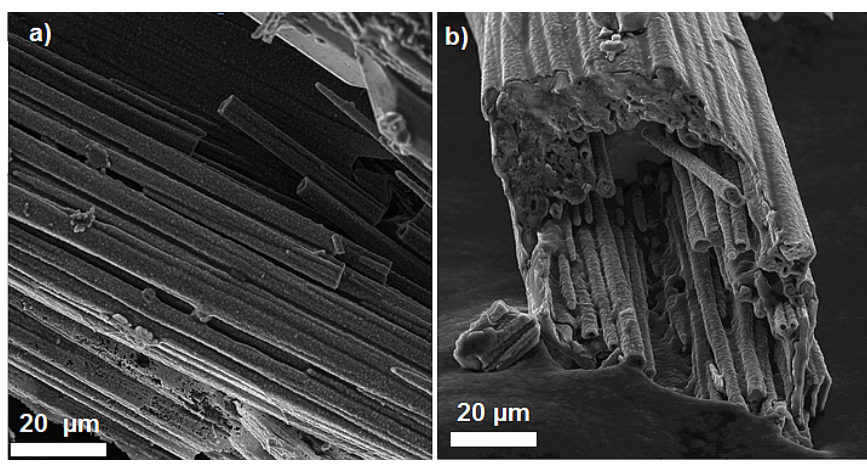


Figure 14. $[RMIm]BF_4$–$Na[SiF_6]$ of mechanically cleaved hollow tubular crystal structures.

- In addition to the new type of hybrid crystals, it can be concluded that the main inference of this paper is that moisture and water sensitive flouroborate type ionic liquids are not suitable for synthesizing hybrid materials via aqueous sol-gel reactions.

5.4. Different shape and sized sol-gel materials (Paper 2)

To find synergy between ionic liquids and metal alkoxides through sol-gel chemistry, it was necessary to expand the understanding of the formation processes of sol-gel. It is reported that an sol-gel approach is used to forming TiO_2 microroll structures by gel film layer obtained from $Ti(OBu)_4$ [72]. While this method is analogous to the aforementioned in its nature, it differs by being simpler as almost no sophisticated material shaping methods and devices are necessary. Also, the preparation method of microrolls from gel layers is far more difficult to control for the preparation of uniform shape structures with precise dimensions as the division of film into segments that roll subsequently is achieved by film cracking. This phenomenon can be taken as a spontaneous process that is inevitably not controllable to full extent. The goal of this study was to expand the knowledge and to influence the size of obtained rolls using special devices to obtain controlled shape and sized structures [6].

Using metal alkoxides as precursors, sol-gel transformation processes can lead to various shapes and sizes of obtained materials. In the present paper formation of tubular microstructures by gel sheet rolling is described. $Zr(OBu)_4$ has been mainly used as the precursor compound in self-formation driven sol-gel preparation sequence that involves gelling the surface of concentrated sol, formation of gel film segments by gel cracking and spontaneous rolling of obtained gel film segments. $Zr(OBu)_4$ was chosen due to the higher viscosity and faster reaction time than Ti analogues [72]. As it was shown in paper the precursor was partially hydrolyzed at R=0.8 to obtain a gelation precursor. Two partially hydrolyzed molecules can link together in condensation (alcoholysis) reaction (section 2.3.). Therefore the equimolar amount of water is not necessary for the completion of sol-gel process. The dependence of gel film rolling diameter on several system parameters was estimated and the nature of observed sol-gel processes was also discussed in this study.

Major results in this study can be concluded.

- A device was designed based on a rotating cylinder situated in an isolated chamber to evaluate the dependence of gel film thickness and rolling diameter on various parameters (Figure 15). The precursor was distributed on the outer surface of the moving cylinder as a solution of suitable viscosity. The solvents were then removed by vacuuming while the cylinder was continuously rotated to obtain a still layer, followed by gel film formation by exposure to humid air after removing the isolating cover.

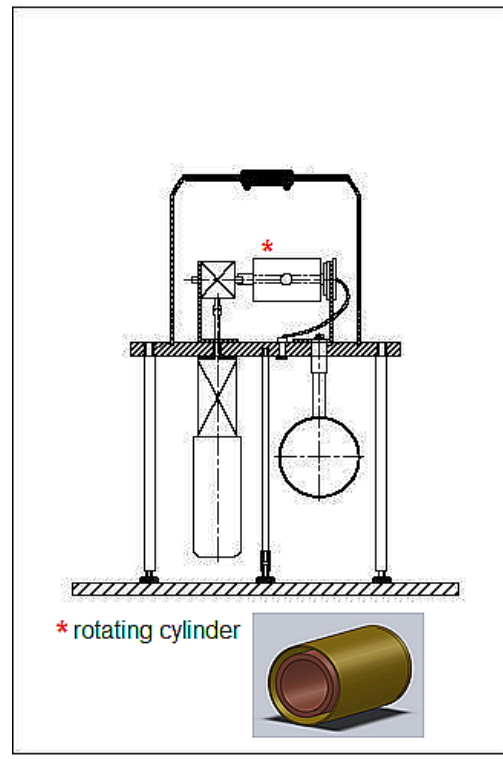


Figure 15. A unique chamber, to synthesize microtubular structures with controlled parameters.

- Applying phenomena that are conventionally considered unwanted (cracking and/or mechanical stress) can lead to spontaneous formation of gel sheets rolled into microtubular structures (Figure 16).

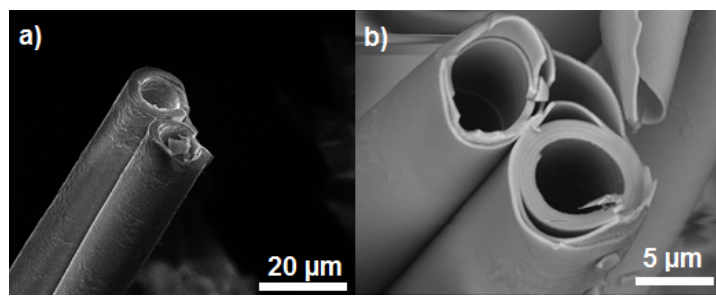


Figure 16. Gel sheets rolled into microtubular structures. a) tublar structures of $Ti(OBu)_4$; b) tublar structures of $Zr(OBu)_4$.

- The principal reason for self-rolling is mechanical stress gradient in the gel film (presented schematically in Figure 17). Concentrated sol as the precursor in the process was used and the reactivity of used precursor materials, $Zr(OBu)_4$, $Ti(OBu)_4$, and $Hf(OBu)_4$), is relatively high. The diffusion depth of hydrolyzing water molecules, that causing hydrolysis that leads to gelling is low and gelation is limited to the surface layers. As the metal alkoxide precursors are exposed to humidity, hydrolysis, polymerization, and solvent evaporation processes take place in these materials. So the material also becomes increasingly denser and the diffusion of water molecules through the gel layer formed on the surface into deeper material is additionally prevented even further. It can be concluded, that the densification speed is the highest on the surface and decreases in deeper layers. It is showed that relatively high humidity is needed for effective gel film formation and subsequent rolling formation which also contributes to quick surface gelation. Therefore, a gradient in gelation extent is expected to be established in upper layer of the material [6;73].

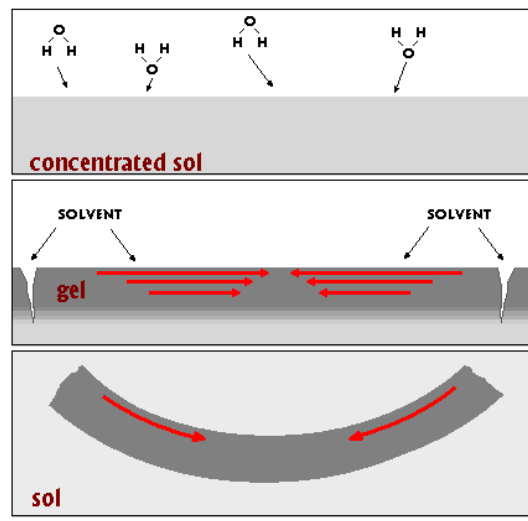


Figure 17. Scheme of gelation processes of concentrated metal alkoxide sols [6;73].

- To release the freestanding gel film sheets, the remaining sol under the gel layers is dissolved. Therefore less polymerized layers can also be expected as the porous material that is not entirely gelled can absorb solvents. If present, this effect would lead to material to expansion in the bottom layers of the gel film, while causing considerably smaller changes in the upper, fully gelled layer.

- Generally, precursor mixing in the surface layer during exposure and gelling must be minimized for gelation, the mobility of molecules has to be low enough to restrict gelation processes to the surface layer for as large extent as possible. Using low solvent concentration in the precursor, partial polymerization of the precursor or choosing a precursor compound that already has high viscosity is possible to restrict gelation processes to the thin surface layer.

- Based on previously described mechanisms in order to gel only the surface layer, the reactivity of the precursor has to be high. The water molecules from the gas environment above the precursor layer would then react with precursor molecules in the surface layer. To accomplish this, precursor compounds that have suitably high hydrolysis reaction speed should be preferred and the initial extent of precursor polymerization should be kept minimal as reaction speed of partially hydrolyzed metal alkoxides is significantly lower.

- Film thickness of obtained gel rolls as well as the inner diameter was characterized by averaging over 30 rolled structures measured in SEM as relatively small number of roll structures could be produced in one cycle on used device. A power-law trend in thickness and rolling diameter dependence on the exposure time was still evident (see Figure 18. and 19.).

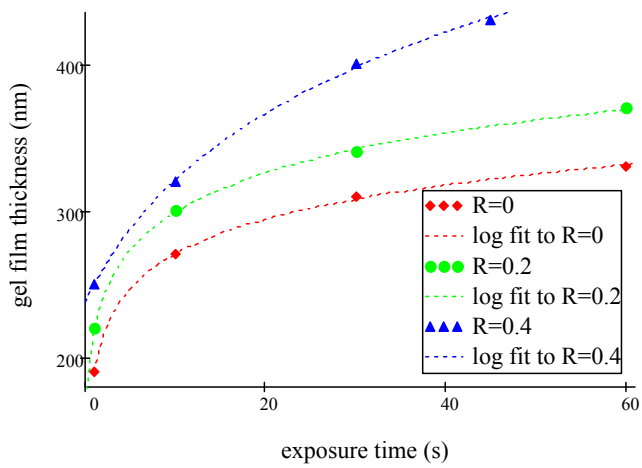


Figure 18. Gel film thickness dependence on the exposure time of humid air (28% 21 ^{o}C) [6;73].

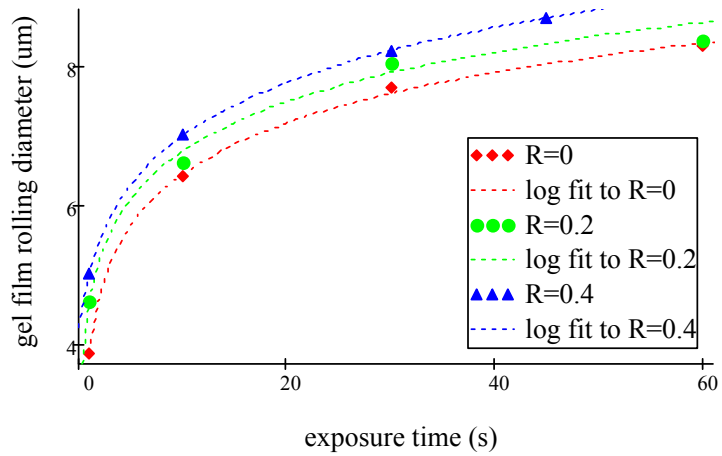


Figure 19. Gel film rolling deameter dependence on the exposure time of humid air (28% 21 ^{o}C) [6;73].

- Several series of experiments were carried out varying the R value of $Zr(OBu)_4$ precursor and the time of exposure to humid air on the experimental device based on rotating cylinder. Gel film thickness of obtained gel rolls as well as the inner diameter directly depends on the exposure time of humid air. Relations in Figure 18. and 19. can be explained by diffusion of water. As the gelling starts from the surface, an increasingly thick layer of gel is formed that inhibits the diffusion of additional water molecules to deeper material layers and removal of the solvent generated in the gelling process [73]. In Figure 20 it is showed the dependence of rolling diameter and film thickness in experiments with different R values. Therefore it can be concluded, that formation of gelling extent gradient is freestanding from the extent of initial hydrolysis of the precursor.

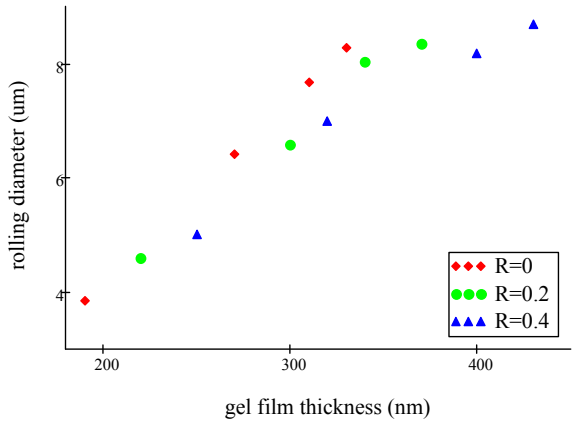


Figure 20. The relation between gel film thickness and rolling diameter [6;73].

- The analysis of experimental data could provide much more valuable information about the gelling processes in general. The conclusions based on the estimating results described hereby would have to be regarded as speculations. The decrease in gel film thickness growth speed is showed, but in certain point gel film thickness is too great to form whole roll-structure (exposure time of humid air was too long, only partially curled relatively thick film segments were obtained, Figure 21).

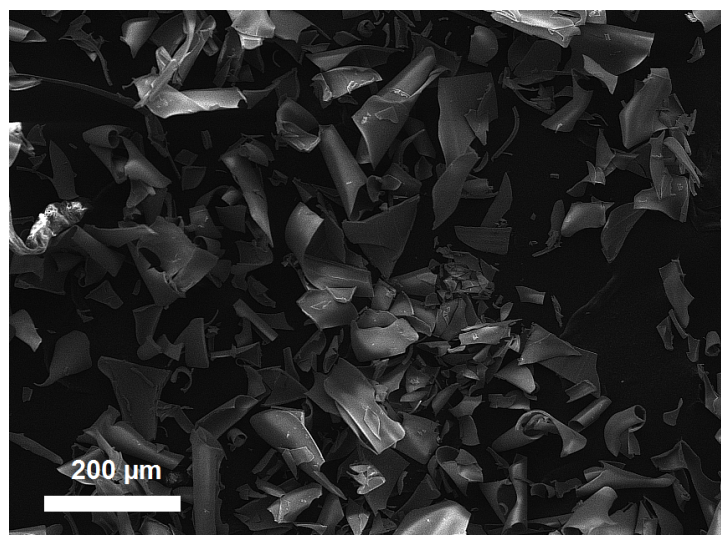


Figure 21. Half –roll gel stuctures of $Zr(OBu)_4$. The film thickness is too great to form whole roll structures.

- The microtubular structures studied in presented work have not been tested in direct applications. Ti, Zr and Hf oxides have high melting temperatures, chemical resistivity, catalytic activity, mechanical hardness, optical transparency, good thermal and electrical isolation properties as well as biocompatibility. Potential applications can be based on these spectacular properties and due to their size and unique shape. Controlled release carriers, catalysts, filters, chemical na thermal environment, optical microsensors, optical resonators, insulating materials or biomaterials can be suggested [6].

5.5. Homogeneous hybrid ionogels (Paper 3)

In creation of ionic liquid-sol-gel hybrid materials ionic liquids are used as nano-pore templates inside a host matrix. That approach allows using sol-gel method to synthesize TiO_2 nano-particles (used in photocatalytic reactions) that have greater specific surface than analogues where synthesis does not use ionic liquids.

$Ti(OBu)_4$ as a precursor was chosen due to its properties and potential applications in a field of textiles which are described in the next section. The mechanisms of the formation of fine metal oxide fibers or microtubes compared to the solidification of pure metal alkoxide precursors, enabling transformation of liquid threads into solid material have been shown previously [74]. In the same work it is shown that the metal-oxo-alkoxide liquid threads were, immediately jacketed by a solid shell that formed on the outer surface via hydrolysis–condensation of the precursor, when pulled out from the bulb into a humid atmosphere. The coalescence of the resulting nanoparticles from Ti-alkoxides is described as response to a densification of material resulting from the evaporation of the alcohol released during the reaction process. The drying process in Ti-alkoxides is much more controlled, elastic and homogeneous than Zr analogues. Using ionogels, the material shrinkage and fluctuation is even much more lessened. The combination of metal alkoxide and ionic liquid is beneficial, because ionic liquid behaves as a coordinating plasticizing agent, and the evaporation of ionic liquid is not taking place. Functionalized ionic liquid can act as a covalently bonded medium. Consequently the sol-gel materials made by ionogel, enables to avoid cracking, which is unfortunately common for sol-gel materials in the middle of the shrinkage process.

The major results can be concluded:

- It was described that floroborate or florophosphate type ionic liquids are useless or even dangerous in described composites due to their changes in the structure at ambient conditions. Solution is to embed ionic liquid into the host matrix without leaking but on the other hand, it is hard to solve the problem of mixing polar ionic liquid and nonpolar metal alkoxide without chemical modification. In this study, three imidazolium and tetrafluoroborate based ionic liquids $[EMIM][BF_4]$,

[BMIM][BF_4] and [DMIM][BF_4] were combined with titanium(IV) butoxide. The obtained ionogel was formed into fibers but the polar and nonpolar phases were separated. As a result, two types of hybrid materials were synthesized. Depending on concentration of ionic liquid in composites different pores up to 1 μm in diameter, and channels up to 1 cm in length and 300 nm in diameter were obtained in metal oxide matrix (Figure 22). It was observed that ionic liquid is not stabilized in the host matrix and shows also tendency to leak while the obtained fiber is drying.

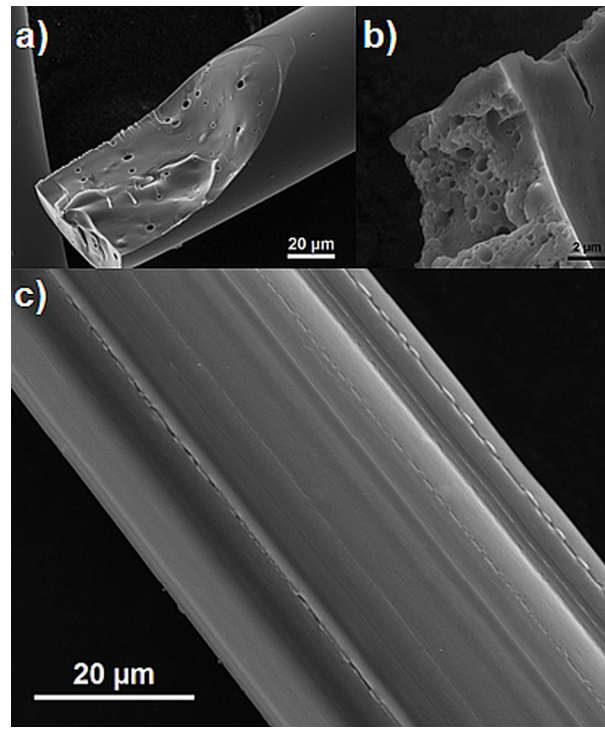
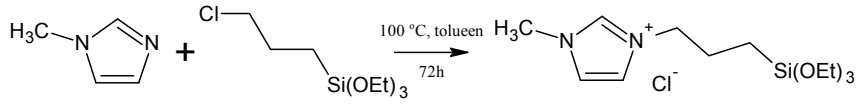


Figure 22. SEM images of different mechanically cleaved gel fibers: (a) a gel fibers synthesized, using [EMIM][BF_4] (9.4% w/w), pores are seen; (b) using [DMIM][BF_4] (8% w/w) ,pores are seen; (c) using [EMIM][BF_4] (1.7% w/w), channels are seen [76].

- To obtain homogeneous solutions, functionalized ionic liquid - 1-methyl-3-[3'-triethoxysilyl)propyl]imidazolium chloride (MTICl) salt was formed through quaternization of *N*-alkylimidazole with suitable silyloxo functional reagent but as significantly higher temperatures are necessary the yields are lower as possible side reaction can occur [7;75] (Scheme 3.).



Scheme 3. Synthesis of MTICl. Ionic liquid was prepared using 1:1 mole ratio of 1-methylimidazole and 3-chloropropyl triethoxysilane through one step synthesis [76].

The structure of the product was confirmed by NMR and FTIR. Although the synthesized ionic liquid was yellowish, analysis did not indicate any impurities and the yield of synthesis was comparable with the results of other authors [7;76]. The main advantage of MTICl over [EMIM][BF_4] and [DMIM][BF_4] is derived from its chemical structure. MTICl is miscible and reacts with titanium alkoxide during the sol-gel process and therefore the ionic liquid was covalently immobilized to gel structure. Ti-oxo-alkoxide and ionic liquid form a covalent network and as a result it is possible to obtain stable and homogeneous materials from titaniumtetrabutoxide and MTICl through the aqueous sol-gel reaction. Functionalized ionic liquid can be involved in the sol-gel processes through ethoxy groups and associate with titanium alkoxide network forming Si-O-Ti covalent bonds. As a result, in the obtained hybrid material MTICl is covalently bonded through the cation with titanium alkoxide network and therefore possible leakage of the confined ionic liquid is prevented (Figure 23.).

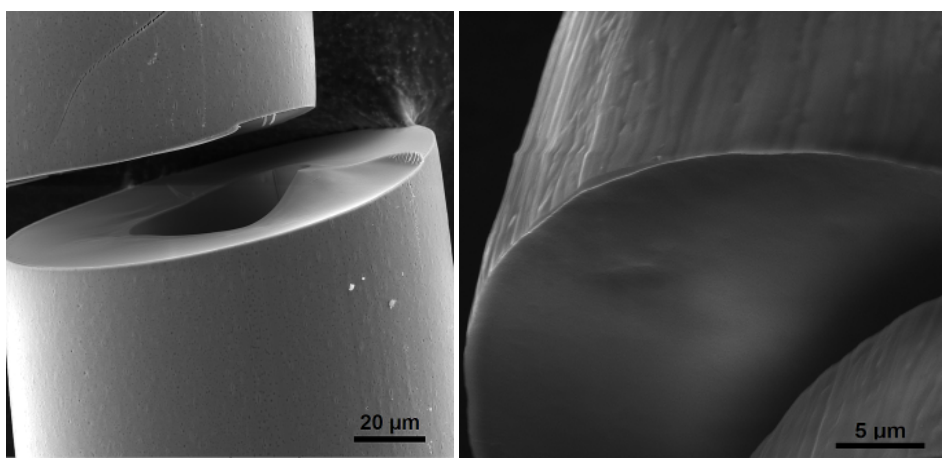
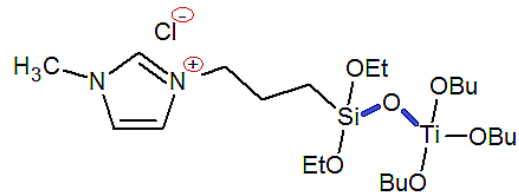


Figure 23. Different shaped ionogel materials. Homogeneous ionic-liquid – Ti-oxo-alkoxide tube (left); homogeneous ionic-liquid – Ti-oxo-alkoxide fibre (right).

- Si-O-Ti covalent bonds were proved using direct and indirect methods. EDX measured using several different zones of the fibers and using different energies (5-15kV). The results were coincident and showed micro homogeneity and detected ionic liquid both inside the fibers and on its surface. Solid phase ^{29}Si NMR analysis showed that MTICl is involved in sol-gel processes through the ethoxy groups and as a result it associates with the titanium alkoxide network by covalent bonding. Based on the model (chemical shifts ($SiO_{(2-2x)}C_{(x)}$)) mentioned in literature previously [77], the spectrum signals range at SiC_2O_2 and $SiCO_3$. To predict Si-O-Ti bond infrared frequency the density functional theory (DFT) calculation was performed using the GAUSSIAN 09 software with B3LYP functional and 6-31G basis set. For frequency estimation, one of the simplest configurations of molecular structure, which could hypothetically be formed in our MTICl/$Ti(OBu)_4$/H_2O system, was chosen. The model compound used in calculations is shown in Scheme 4. For such system program predicted intense vibration at 1039 cm^{-1}. According to measured result in this work, the peak was at 1042 cm^{-1} in IR spectrum of the MTICl containing fibers.



Scheme 4. Molecular structure used in GAUSSIAN 09 program for Si–O–Ti bond IR frequency calculation (Et and Bu are ethyl and butyl groups, respectively) [76].

5.6. Ionogels and textiles, properties and applications (Paper 4)

Sol-gel technique offers various possibilities for creating new surface coatings with different functional properties. Sol-gel technology gives us possibility to design surface properties by combining specific characteristics of different chemical compounds in a single composite material. At the same time the application of sols can be put into practice with techniques commonly used in the textiles industry. Sol-gel method is suitable for obtaining a wide range of functionalized textiles, although, many properties of different metal alkoxide precursors vary to some extent. Titanium tetrabutoxide was chosen due to its properties and potential applications which were mentioned in literature previously [78;79;80]. For textile coatings $Ti(OBu)_4$ is suitable due to the lower viscosity and lower reaction time than Zr and Hf analogues. Also, titanium alkoxide thread shrinking is three times lower than analogues [81]. In addition,

no coordination number change is characteristic to Ti-alkoxides during the shrinking [72;82].

TiO_2 is well known oxide because of its properties like UV protection, photocatalytic ability and biocidal characteristics [83;84].

Described in section 5.5., titania-gel fibers were formed directly by pulling oligomeric mass in humid air using borosilicate glass stick. Exposing the pulled fibers to air resulted in immediate formation of thin solid layer on the materials surface due to polymerization caused by water vapour in the air. Dimensions of the fibers depend greatly on the viscosity of the precursor, humidity of the surrounding atmosphere, and pulling speed.

Titania or titania/silica oxide fibers with very fine diameters of about 100-200 nm can also be prepared by electrospinning of Ti-, Si- or Ti/Si - alkoxide composite precursors [85:86]. Electrospinning is an versatile electrostatic fiber fabrication technique. Although in described work obtained fibres are very thin, they are stable in a calcination process from 500°C up to 1200°C.

Directly synthesized metal-alkoxide fibers used as a textile tensile are rather rare in the literature. The properties of these materials are promising, but they lack flexibility and stiffness compared to organic or inorganic textile materials. Therefore, it is beneficial to use already existing materials and give them novel and useful properties through the functionalization. Method for coating textile fibers is frugal in its nature, being simpler as sophisticated material shaping methods and devices are not necessary [87].

- Simple equipment for separation of carbon nanotube “bucky gels” have been elaborated (Figure 24). The main intention for preparation of this equipment was to create a special device, where ionogel-carbon nanotube mixture can be blended and separation of nanotubes was facilitated applying the mechanical force between two glass plates. The idea was to use vacuum and gas resistant chamber where fixed and rotating glass plates settled together. Rotating speed is controlled through the special servo-motor, controller has the opportunity to vary the rotation speed from 1 rpm to 3000 rpm. On this apparatus it was possible to show the separation of carbon nanotubes.

  Uniform dispersion of ionic liquid in the mixture lead to exfoliation of the CNT ropes without any sonication. Fukushima et. al. showed that ionogels are formed by physical cross-linking of the single walled nanotube bundles, mediated by local molecular ordering of the ionic liquids rather than by entanglement of the nanotubes, but nowadays there is an on-going discussion about the mechanism of the interactions between IL and CNTs [88].

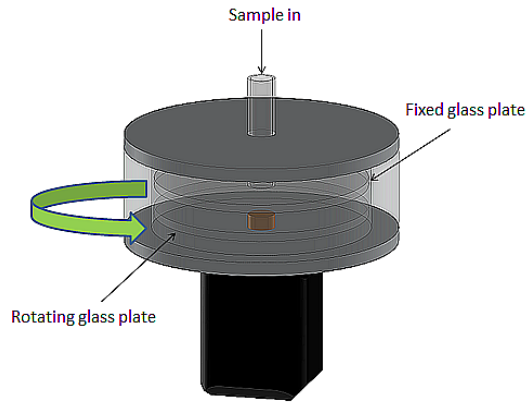


Figure 24. A equipment for mixing "bucky gels". The sample is mixed in a vacuum tight chamber, between two glass plates [88].

- Addition of CNTs improves the mechanical properties of cotton fibers, but may improve electrical properties as well. Also, as it was mentioned in paper, electrical measurement results should be taken as a rough estimation demonstrating the general nature of the system (same system is used for cotton fabrics), rather than the exact measurement.
- Several series of experiments were carried out varying the concentration values of ionic liquid-metalalkoxide and carbon nanotube mixtures. The time of exposure to the reaction was same in all cases. Linear density (Tt), breaking force (Bf), ultimate strength (Us) (breaking tenacity), as well as particular swelling capacity of cotton yarns as dimensional stability were measured by averaging results of several cotton yarns measured (Table 1.). It can be concluded that reaction of cotton OH groups with BuOTi is preferred to EtOSi due to the faster reaction time of metal alkoxide. The major difference in reactivity of metal alkoxides from those of silicon is due to their very easy and rapid reaction with water in the absence of catalysts. The reaction times for hydrolysis of titanium alkoxides are 10^5-10^8 times faster than silicon alkoxides [89]. The combination of metal alkoxide and functionalized IL is beneficial, because IL behaves as plasticizing agent creating stronger, crack free, hydrophobic, and more stable coatings for fibers. Moreover, organic modification reduces the collapse of pores and the formation of cracks (Figure 25).

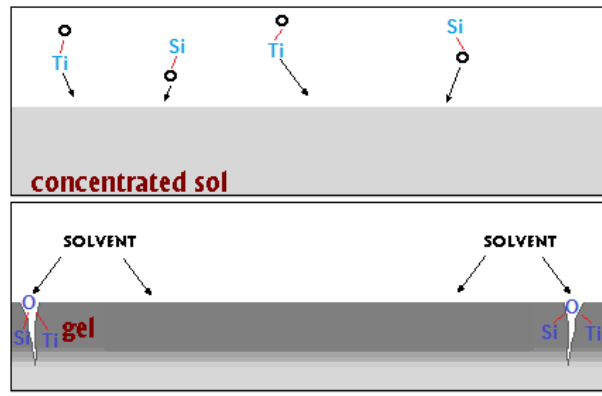


Figure 25. Graphical description of covalent bond formed in precursor material.

- The presence of hydrophobic $Si(OEt)_3$ groups contributes hydrophobicity on the cotton hybrids and consequently weight and volume variation is very low. The hydrophobic nature and thermal stability of these new hybrid cotton materials make them suitable for preparation of packing or insulating materials. Dimensional stability in the presence of water was ascertained by weight (ΔW) after submersion of sample in water for 24 h at room temperature. Non-treated cotton fibers increased its weight by 286 %. Ionogel treated cotton fibers are more stable in the water, especially the hybrids prepared with uniformly dispersed CNT network around the fibers.

Table 1. Different physical properties of chemically modified cotton treads [88].

Material	C°	MTICl %	ΔW%	Tt (Tex)	Bf (N)	Us (cN/Tex)
Cotton treads (Ct)	21 two weeks	-	286	36 ± 3	4.7 ± 0.1	13.0
Ct+MTICl/ $Ti(OBu)_4$	21 two weeks	3	51	57 ± 3	8.8 ± 0.2	15.4
Ct+MTICl/ $Ti(OBu)_4$	21 two weeks	8	45	59±3	9.4 ± 0.2	15.9
Ct+MTICl/ $Ti(OBu)_4$	21 two weeks	12	28	61±3	10.3 ± 0.2	16.9
Ct+MTICl/ $Ti(OBu)_4$	100 4 h	12	34	49 ± 3	7.5 ± 0.2	15.3
Ct+MTICl/ $Ti(OBu)_4$+CNTs	21 two weeks	8	20	62± 4	12.2 ± 0.3	19.7
Ct+MTICl/ $Ti(OBu)_4$+CNTs	100 4 h	8	26	56 ± 4	8.9 ± 0.3	15.9
Ct+ $Ti(OBu)_4$	21 two weeks	-	180	55±3	7.9 ± 0.2	14.4
Ct+MTICl	21 two weeks	-	32	45 ± 3	5.9 ± 0.1	13.1

SUMMARY

(Developement of ionic liquid composites by sol-gel method for elaboration of industrial nano- and microstructures)

The main aim of this research was to develop methods of synthesizing ionic liquid/oxide composites based on ionic liquids and metal alkoxides, and to clarify/find out properties and applications of formed structures. The topic of the thesis – combining ionic liquids and sol-gel method to create functional composites – is a relatively new research topic and has only been developing during last decade. Ionic liquids are chemically rather inert, thermally stable materials with ionic conductivity. The class of materials is highly popular because of the rather low production costs and the simplicity of synthesis methods, which induce extra competitive alternative for production of conductive and/or transparent electrolytes, nanoparticle synthesis, or functionalized textiles for different applications.

One of the main innovative contribution to the field of research from this work is the developed competence which allows to explain sol-gel processes during the synthesis of different size and shape materials, polymerization of ionic liquids, and condensation in oxide matrix to improve the stability of this nanocomposite (usually ionic liquids tend to leak out of the material), and application possibilities of novel materials.

Main results from this work:

– It was shown that ionic liquids containing BF_4 anions hydrolyze in humid environment at the room temperature. Novel hybrid dual-component crystals were discovered for the first time, which formed during the hydrolysis when in contact with other substances (e.g. glass, oxides, ceramics). Novel clustered structures were described using electrostatic interaction model where negatively charged fluorine atoms interact with positively charged imidazolium ions of ionic liquid. From this it was concluded that ionic liquid is the binding element in the formation of two component crystal structures. This phenomenon is mainly attractive because of its novel conceptual value, but is also a warning that even short-time experiments might be affected by the reactions between the ionic liquid and the surroundings.
– A method to obtain rolled structures from self- rolling gel sheets was developed. A theory was proposed about gel film self-induced fracturing and the underlying reason for self-rolling by mechanical stress gradient was given. Options to vary shape and size of ceramic structures were estimated changing composition of reactants and synthesis methods. Synthesized materials showed high thermal endurance and a possibility to have metal oxide structures.
– Time-independent mixtures of ionic liquid and alkoxides (ionogel) were obtained and it was shown that the distribution of components is homogeneous. Stability of a material is explained by covalent Si-O-Ti bond between ionic liquid and metal alkoxide. Synthesized precursors were used

to produce different size and shape ceramic materials mostly without defects. Materials prepared by sol-gel method have characteristics to crack and creation of defects. These processes are minimized in ionogels due to ionic liquid's effect on orientation and plastification of the structure of a material. Also, ionic liquid with non-existent vapour pressure does not vaporize which prevents stress in aging material.

- Synthesized mixtures of ionic liquid and metal alkoxide were implemented in developing functionalized textiles. It was shown that cotton threads treated with ionogel have better breaking strencht, hydrophobic qualities, and wearproof compared to starting material. After chemical modifications, material qualities never deteriorated even after repeated washing with water.
- Novel carbon nanotube – metal alkoxide – ionic liquid gels were developed where ionic liquid coordinates carbon nanotube movement from aggregate inside a material. Electric properties of material increased when synthesized mixtures were in functional state (films, fibers).

SUMMARY IN ESTONIAN

Ioonse vedeliku komposiidi väljatöötamine sool geel meetodil tööstuslike nano- ja mikrostruktuuride saamiseks

Töö eesmärgiks oli ioonsetel vedelikel ja metalli alkoksiididel põhinevate ioonvedelike/oksiidide koposiitide sünteesimeetodite väljatöötamine ning saadud struktuuride omaduste ja rakenduste selgitamine. Doktoritöö teemaks oleva ioonsete vedelike ja sool-geel meetodi kombineerimine funktsionaalsete komposiitide loomisel on alles viimasel kümnendil kujunenud teadussuund. Ioonsed vedelikud on keemiliselt üsna inertsed, suurepärase temperatuuritaluvuse ning ioonse juhtivusega ained. Suur huvi antud materjalide klassi vastu on seotud nende madala omahinna ja valmistamismetoodika lihtsusega, mis tekitab äärmiselt konkurentsivõimelise alternatiivi juhtivate ja/või läbipaistvate elektroodide, nanomõõdus osakeste sünteesi või funktsionaliseeritud tekstiili valmistamiseks erinevates rakendustes.

Töö üheks põhiliseks panuseks antud teadussuuna arengule on kompetentsi loomine, mis võimaldab innovatiivselt selgitada sool-geel protsesside olemust erineva suuruse ja kujuga materjalide sünteesil, ioonsete vedelike polümerisatsiooni ja kondensatsiooni läbiviimist oksiidses maatriksis. Töö tulemi abil parendati sellise nanokomposiidi stabiilsust (ioonsed vedelikud kipuvad reeglina ainest välja lekkima), ning väljundina näidati uudsete materjalide potentsiaalset tööstuslikku rakendamist.

Töö peamised tulemused on:

– Näidati, et BF_4 aniooni sisaldavad ioonsed vedelikud hüdrolüüsuvad niiskes keskkonnas toatemperatuuril. Olles hüdrolüüsumise käigus kontaktis teiste materjalidega (nt. klaas, oksiidid, keraamika) avastati esmakordselt uudsete hübriidsete kahekomponentsete kristallide teke. Liitstruktuure kirjeldati elektrostaatilise interaktsiooni mudeliga, kus negatiivselt laetud fluoori aatomid interakteeruvad ioonse vedeliku imidasooliumi positiivselt laetud ioonidega. Sellest järeldati, et just ioonne vedelik on siduvaks jõuks selliste struktuuride kokku kasvamisel liitkristalliks. See nähtus on huvitav eeskätt oma uudsete tunnetuslike väärtuste poolest, olles ühtlasi hoiatuseks, et ka lühemaajalised katsed võivad olla häiritud ioonse vedeliku reaktsioonidest ümbritseva keskkonnaga.
– Töötati välja meetod geelkile fragmentide rullumiseks metallialkoksiidi kontsentreeritud soolist sool-geel meetodil. Püstitati teooria geelkile iseeneslikust pragunemisest ning mehaaniliste pingete mõjul geelkile fragmentide spontaansest rullulisest sool-geel meetodile iseloomulike protsesside tõttu. Muutes lähteainete koostist ning valmistusmeetodeid, hinnati võimalusi keraamiliste struktuuride kuju ja suuruse varieerimiseks. Sünteesitud materjalid näitasid kõrget temperatuuritaluvust ning võimalust viia struktuurid keemiliselt oksiidsele kujule.

- Valmistati ioonsest vedeliku ja metalli alkoksiidi segust (ionogeelist) ajas stabiilsed materjalid ning näidati segu koostisosade homogeenset jaotumist. Sünteesitud prekursoritest valmistati erineva kuju ja suurusega keraamilisi materjale. Sool-geel meetodil valmistatud materjalide omaste pragude ja defektide suurus ning jaotus on minimaliseeritud tänu ioonse vedeliku orienteerivale ja plastifitseerivale mõjule materjali struktuuris. Lisaks olematu aururõhuga ioonne vedelik ei aurustu, mille tulemusena välditakse geeli vananemisel tekkivaid pingeid.
- Rakendati sünteesitud homogeenseid ioonse vedeliku ja metallialkoksiidi segusid funktsionaliseeritud tekstiili valmistamisel. Näidati, et ionogeeliga töödeldud puuvilla kiududel suureneb tõmbetugevus, hüdrofoobsus ning kulumiskindlus võrreldes algse materjaliga. Tänu keemilisele modifitseerimisele ei täheldatud materjali omaduste halvenemist ka korduval pesemisel veega.
- Töötati välja uudsed süsiniknanotoru-metallialkoksiidi-ioonse vedeliku geelid, milles ioone vedelik koordineerib süsiniknanotorude agregaadist laiali viimise maatriks-materjali sisemusse. Sünteesitud segude viimisel funktsionaalsele kujule (kiled, fiibrid) suurendati materjali elektrilisi omadusi.

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I. **Välbe**, **Raul**; Tarkanovskaja, Marta; Mäeorg, Uno; Reedo, Valter; Hoop, Andres; Kink, Ilmar; Lõhmus, Ants. Elaboration of hybrid cotton fibers treated with ionogel/carbon nanotube mixture using sol–gel approach. *Central European Journal of Chemistry.* **2014,** [accepted].

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VII. Invention: Method for synthesiz of stabilized oxide nanometric size particles in ionic liquids; Owner: University of Tartu and Estonian Nanotechnology Competence Centre; Authors: **Välbe**, **Raul**; Lõhmus, Rünno; Tarkanovskaja, Marta; Mäeorg, Uno; Reedo, Valter; Umalas, Madis; Kübarsepp, Jakob; Lõhmus, Ants.

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I. **Välbe**, **Raul**; Tarkanovskaja, Marta; Mäeorg, Uno; Reedo, Valter; Hoop, Andres; Kink, Ilmar; Lõhmus, Ants. Elaboration of hybrid cotton fibers treated with ionogel/carbon nanotube mixture using sol–gel approach. *Central European Journal of Chemistry.* **2014,** [aksepteeritud].

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DISSERTATIONES SCIENTIAE MATERIALIS UNIVERSITATIS TARTUENSIS

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