



**DUTCH-BELGIAN BEAMLINE  
AT ESRF**

**EUROPEAN  
SYNCHROTRON  
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## **Experiment Report Form**

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

(next page)



	Experiment title: <b>Tailoring structural evolution of energy-efficient molecular separation membranes with SAXS</b>	<b>Experiment number:</b> <b>26-02-465</b>
<b>Beamline:</b> BM-26B 'Dubble'	<b>Date(s) of experiment:</b> From: 11-7-2009 To: 16-7-2009	<b>Date of report:</b> 12-8-2009
<b>Shifts: 12</b>	<b>Local contact(s):</b> dr. G. Portale	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>H.L. Castricum* (Universiteit van Amsterdam), J.E. ten Elshof*, S. Khan*, S.A. Veldhuis*, T. Stawski*, R. Besselink* (Inorganic Materials Science, Universiteit Twente), J.F. Vente (ECN)</b>		

### **Report: (max. 2 pages)**

Substantial energy savings are anticipated by the implementation of membrane technology in molecular separation processes. By replacing notoriously energy-inefficient processes such as distillation and cryo-distillation, yearly energy reductions can be effected of several hundreds of millions of barrels of oil. Among all available materials, a hybrid organic-inorganic material has shown the most promising prospects by far for actual industrial application. The selective membrane material consists of a thin film of sol-gel organosilica with a narrow nanopore (< 1 nm) size distribution dipcoated onto a support. The material is prepared from ethane-bridged silsesquioxane precursors and combines molecular separation selectivity with high structural stability. We have shown that this membrane is exceptionally stable in water at 150°C for at least two years [1-3]. More recently, we have been able to increase the pore volume, and thus obtained an advantageous combination of high selectivity and high permeability towards the dehydration of *n*-butanol. A high permeability minimizes the required membrane surface, module size, and thus the cost. We demonstrated good acid stability, allowing effective application of the membrane in dewatering processes under conditions close to the ones required in industry [4]. To obtain these results, we have used SAXS for characterization and tailoring of the colloidal sol used for membrane coating [5].

In order to actually replace existing energy-inefficient technologies, the membrane has to show commercial potential. This requires the demonstration of a number of challenging separations, including the selective dehydration of ethanol and methanol as well as highly selective separation of hydrogen. For this, we need better control over the nanopore size. The strategies that we intend to use include variation of the size of the organic bridging group, the introduction of metal alkoxydes with a different coordination number, and adaptation of the reactant composition of the sol. However, the relation between these strategies and the ultimately obtained nanopore structure is highly complex, and to a great extent determined by the applied drying procedure. Detailed understanding of this drying stage is therefore needed to allow effective tailoring of both the pore size and pore volume of organosilica thin films.

Network formation during drying and the subsequent microstructural development towards a solid gel is determined by three main factors. One involves the intrinsic reactivity of the precursor, one the concentration increase of the various reactants upon solvent evaporation, and one the actual surface charges in the sol, determined by both the colloidal structure and the acid concentration. To allow further tuning of the pore structure, we need to systematically assess which factors dominate at what stage and how these influence the

structure. The high intensity of a synchrotron beam is ideal for studying the rapid structural evolution on a second-to-minute scale, using SAXS to study the drying process of a thin layer. In this way, a deeper understanding of network formation during rapid drying can be acquired. Better understanding of these processes will allow a more rational membrane design by recognition of the parameters that can be tuned. We can thus improve and optimize the structure, and thus the separation performance. This will allow the development of practically applicable membranes to be greatly speeded up.

We have carried out Small-angle X-ray scattering (SAXS) measurements at the DUBBLE beamline BM-26B on (organo)silica sols with various stages of development. We obtained data at short detector distance and studied silica colloidal sols with different bridging groups. By combining SAXS with other techniques, such as DLS (which determines the hydrodynamic radius of the sol particles), we can obtain a full description of the effect of the organic groups on the development of the structure. We varied independently the catalyst concentration, the hydrolysis ratio and the silane concentration for sols that were introduced in thin-walled glass capillaries. The applied beam energy was 16 keV, and the sample-detector distance 1.5 m.

Thanks to optimized slit settings and focusing on the beam stop and efficient assistance by our local contacts, a high resolution could be obtained, also for capillaries. We experienced a very stable beam delivery throughout the experiment. Excellent reproducibility of the scattering patterns was found, enabling observation of reactant- and catalyst-dependent development of sols, and structural evolution of as-dried films.

The drying step is a very important but almost unexplored stage in the preparation of a sol-gel derived material. The most exciting and interesting part of our experiments were the in-situ drying experiments, for which a special setup has been developed by Guy Eeckhaut and Wim Bras, which we were kindly allowed to use. We successfully attempted in-situ drying experiments of sols using this setup, at various temperatures.

The drying experiments show that a colloidal organosilica sol can form either a microporous or a mesoporous network, both under acid conditions. The exact conditions are strongly dependent on the electronic structure of the precursor. For all precursors, the formation of porosity depends on the availability of water, the acid concentration and the drying temperature. Understanding the development of porosity upon drying is highly relevant for the further development of molecular separation membranes.

The obtained results will allow us to better understand how the colloidal network develops during drying, as well as to relate synthesis conditions to the membrane pore structure and separation performance. Tailoring of the recipe for membrane development can thus be greatly accelerated and will allow faster industrial implementation of membrane technology.

## **References**

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- [2] H.L. Castricum, A. Sah, R. Kreiter, D.H.A. Blank, J.F. Vente and J.E. ten Elshof, *J. Mater. Chem.* **18** (2008) 1
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- [4] H.L. Castricum, R. Kreiter, H.M. van Veen, D.H.A. Blank, J.F. Vente and J.E. ten Elshof, *J. Membrane Sci.* **324** (2008) 111
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