

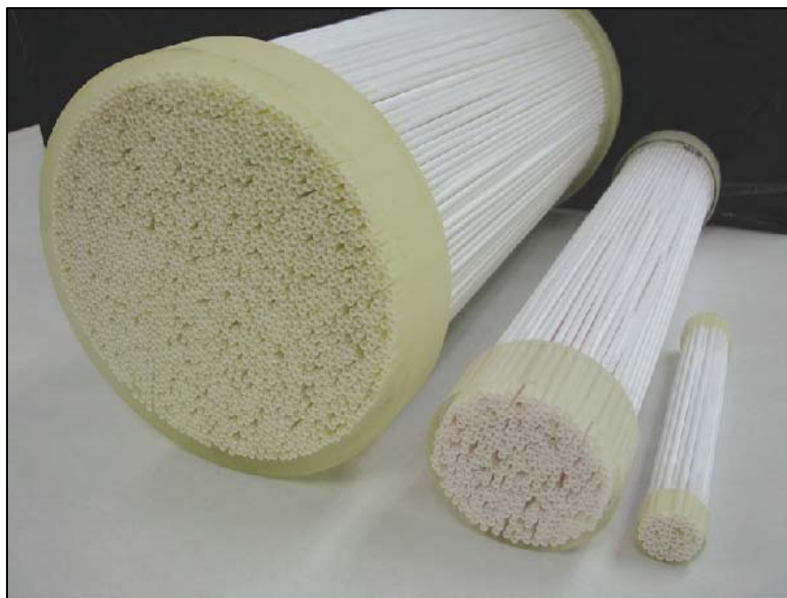
STW Partnership Program Plan
“STW - Hyflux CEPAration Inorganic and Hybrid Membranes”
April 2009

1. Introduction and industrial relevance

The Dutch Technology Foundation (STW) initiated the Partnership Program for stimulating more effective cooperation between industry and academia and STW invited Hyflux CEPAration BV to apply for a participation in the Partnership Program.

The Program is a new initiative in which one industry is invited to propose the program theme, and universities are invited to propose PhD and Postdoc proposals in a tender. The work is carried out under guidance of university professors as well as industry staff, at university lab, industrial lab and practical environment.

The Company CEPAration BV was founded in 2001 as a spin out from TNO-TPD Eindhoven. In 2006 a joint venture was made with Hyflux Singapore. This JV provided Hyflux a footprint in Europe, access to the hollow fibre ceramic membrane technology as well as the potential to further develop this technology.



Hyflux CEPAration InoCep™ commercial inserts with hollow fibre ceramic membranes. The walls of the fibres are porous with fixed pores in the range from 1400 nm down to 20 nm. The present PP focuses on smaller pores, 1 nm and below for nanofiltration, dewatering, desalination and gas separations.

Hyflux Int., a Singapore Public Listed Company, is a leading company in liquid treatment, energy and special products and it constantly develops and acquires new technologies to strengthen its leading position and broaden its market span. The subsidiary Hyflux CEPAration Technologies (Europe) BV in Helmond carries out the R&D on inorganic and hybrid inorganic/organic membrane technology.



InoCep™ insert in stainless steel sanitary housing

Membrane technology is successfully commercialised as a continuous and low energy requiring separation technology for industrial and consumer applications. Due to growing need for separation solutions and energy reduction the market for membranes is growing by 10 % (polymeric membranes) to up to 15 % (inorganic membranes) per annum. 90 % of membrane solutions apply polymeric type of membranes, mostly flat sheet and hollow fibre. Drawbacks of polymeric membranes are limited life time, limited chemical and solvent resistance, inability for use at high temperature and low fluxes for solution diffusion nano-filtration, RO- and gas-separation membranes as compared to open micro-porous membranes.

With the commercial introduction of inorganic membranes in the mid 80's the market span for membrane technology is growing and durable and resistant products have become available.

A real breakthrough for inorganic membranes leading to a substantial market share of 40 – 50 % needs cost effective and compact inorganic products. The Hyflux CEPAration proprietary inorganic hollow fibre membrane technology (InoCep™) offers such compact and cost effective, durable membranes which are being commercialised for micro-filtration and ultra-filtration applications in dairy, beverage and (petro-)chemical industry and gaining a growing market share.

The Program Plan has been developed through discussions with, and contributions from:

- Prof. Freek Kapteijn, Technical University Delft, Catalysis Engineering
- Prof. Matthias Wessling, University Twente, Organic and Inorganic Membrane Technology
- Dr Emiel J.M. Hensen, Eindhoven University of Technology, Schuit Institute of Catalysis
- Prof. Bert de With, Eindhoven University of Technology, Laboratory for Materials and Interface Chemistry and Soft Matter Cryo-TEM Research Unit



InoCep™ micro-filtration system for product recovery

2. Focus, objectives and applications

The focus of the Partnership Program is on membranes which will enable a further break through in enabling applications which need separations on molecular level at ambient and elevated to high temperatures as summarized below:

Micro porous inorganic and hybrid membranes and modules

- using Hyflux inorganic hollow fibre and stainless steel substrates
- with pores in the range of 1 nm and below for molecular separations, out of zeolite, silica, titania, amorphous carbon and hybrid materials and alike, including materials with catalytic and self cleaning ability
- for applications at elevated temperatures above 150 °C
- for applications at elevated temperatures above 250 °C
- for low energy and high flux desalination applications
- as well as methods like Chemical Vapour Deposition and Infiltration to repair large pores and defects which would destroy the selectivity of the molecular separators

A high need and huge market potential for membrane separation technologies exist in the replacement by membrane separations of costly and energy consuming (cryogenic) distillation processes in petrochemical industries and as alternative membranes for desalination processes by dense reverse osmosis membrane. These membranes can also operate at elevated to high temperature and enable combination of unit operations like reaction and separation in membrane reactors. The membrane concept will be based on the cost effective and compact proprietary inorganic hollow fibre membrane concept of Hyflux CEPAration.

3. Scientific challenges

This program addresses some scientific challenges in the area of ceramic and hybrid membranes for various applications and are highlighted as follows.

Zeolite membranes

- Development of closed zeolite coatings without inter-crystalline pores on the Hyflux-CEPARation supports. Initially targeted for single support, later for e.g. bundles of capillaries in one synthesis step. This constitutes the first phase of a scale-up development program.
- Conversion of continuous porous coatings into closed oriented zeolite layers.
- Application targets are the production of ultra-pure water, medical application and hydrogen separation, each with their specific challenge of chemical stability, perm-selectivity and thermal stability, respectively.

Hybrid organic-inorganic membranes

- Manufacture of closed coatings of hybrid organic-inorganic frameworks (HOIFs). This new class of crystalline, nanoporous materials offer theoretically a large potential in separation areas through selective functionalization of the organic or inorganic part and tuning of the pore size. Other acronyms for these materials are MOFs, COFs, ZIFs and coordination polymers.
- The biggest challenge is to understand and control the formation of closed layers of well-intergrown crystals, i.e. the nucleation and growth processes and the adhesion to a surface of a porous support.

Initial stage of precursor formation for micro porous membrane synthesis

- In membrane technology silica is an important material, in particular for nanosize pore membranes. In spite of many investigations on the formation of silica from compounds such as tetra-ethyl orthosilicate (TEOS) and sodium silicate, the precise mechanism of the structure formation remains unclear. Virtually the only technique to analyse the early stages of structure formation is transmission electron microscopy (TEM). In the case of wet processes, an essential feature is the use of cryo-TEM. For the elucidation of 3D structure tomography is indispensable.
- In many cases the time dependence of processes is followed via a process of taking snapshots at various times. For chemical reactions another route is feasible, i.e. by using a tube reactor in which the reaction takes place and freezing the complete reactor, so that analysis of the structure of the precipitate along the reactor tube yields the structure with increasing time.

Ceramic Hollow Fibre geometry

- The ceramic hollow fibre membranes of Hyflux represent a unique geometry and functionality to construct upon new functionalities such as chemical conversions, new molecular separation functions and self-cleaning and self-healing functions. Such new functions can be constructed onto the Hyflux support as thin layers of nanometre thickness. Such layers may span over the porosity as integral thin soft or solid films, or may be grafted onto the ceramic particles following their shape. Preparative techniques such as macromolecular grafting, chemical vapour deposition, layer-by-layer deposition, atomic layer deposition, sol-gel and polymeric thin film processing.

Scale up of preparation and process

- The valorisation of the anticipated research program depends strongly on the potential to transfer synthetic chemistry and materials science concepts into a processing method and production process. For the hollow fibre geometry, one can envision two situations of built-up of new membrane functionality. One in which each fibre attains its new function prior to the massive parallelization inside

a module; or second subsequent to module production. Next to that, the question of applying the function on the inside or the outside, or on both sides, needs attention. Scale-up of preparation and processing concepts need to be energy and material efficient as well as environmentally benign.

Membrane reactor concepts, scaling up, fouling, lifespan

- Years of experience in membrane science technology have demonstrated that a wealth of functionalities can be synthesized with tremendous molecular specificity. Simultaneously, implementation development also shows that the functionality requires a significant reliable life time of more than one to three years in order to be technologically viable. Scientifically elegant concepts of membrane functionality often fail due to detrimental interactions of the constituents of a complex fluid with the surface of the membrane. Research should focus on characterization and synthesis of functionalities that show extended life time. Degradation of performance and functionality - its avoidance and its rejuvenation – requires particular attention. Such issues may be catalyst poisoning, pore blocking by liquid and gaseous trace components to mention only two.

Multisite nanomembrane reactors

- Safer and more sustainable technologies for producing chemicals require modular designs. For instance, parallel small-scale reactors have the advantage of less storage and transport and smaller capital cost to introduce new processes. Scalability is also an advantage. Micro reactors are very suitable to achieve these goals.
- A next step in this field can be made by integrated design of the micro reactor and the catalyst to achieve complex multistep reactions. It is very often not possible to design a catalyst to carry out in one pot a cascade of reactions. An alternative approach is to spatially distribute several active centres on the nanoscale and transporting the reactant molecules over these nanoreactors. In essence, this requires the design of chemical reactors consisting of nanoscale compartments. Micro reactors form an ideal platform to realize this. Membranes at the nanoscopic level will play an important role in this concept, as they are used to bring together gases and liquid, separate products from reactants and provide driving force to chemical reactions beyond thermodynamic limitations. These membranes will be made of inorganic oxides and most likely of crystalline zeolites, because this latter class of materials not only acts as micro porous membranes but also provides stabilization of all kinds of catalytically active ensembles.

4. Fit of research proposals into the program

The research fields and topics are highlighted below. These at the same time are the criteria which will be used to evaluate the proposals, the more criteria that are fulfilled by a proposal the higher the likelihood for funding in this program.

The proposals should address a substantial number of the following aspects:

Aspects related to design, geometry, membrane materials, and pore sizes:

- projects should be based on Hyflux CEPAration hollow fibre membrane substrates, or
- projects should be based on Hyflux stainless steel substrates
- projects can also be based on Micro-porous and nanofiltration membranes based on zeolite, silica, titania, amorphous carbon and alike
- projects can also be based on Hybrid organic/inorganic, mixed matrix membranes
- projects can include Thermo-mechanical modelling for optimal membrane insert design including potting for high temperature applications

- projects can include a detailed study of the formation of synthesis of micro porous membrane including

Aspects related to future production technologies:

- projects should focus on short and cost effective production routes and scalability
- projects must have a clearly demonstrated potential to generate promising new models or instrument prototypes within the life time of the program

Aspects related to applications of the membranes and testing and pilot testing and modelling:

- projects should focus on applications to include desalination or nanofiltration, or dewatering of solvents including bio-fuel, or gas separations and high temperature gas separations
- projects can include research into self cleaning capability, e.g. like titania membranes with catalytic self cleaning activity
- projects can include pilot testing and process modelling with single- and multi-fibre modules
- projects can include research on (Micro-)membrane reactors including for combination of reaction and separation

Aspects related to market potential:

- projects should have a market potential to be evident
- product realisation should have an estimated time to market less than 5 years
- projects should be based on sustainable innovations and have a related optimal energy efficiency

Aspects related to cooperation and size of projects:

- projects must contain excellent scientific research with an innovative approach, and be based on a multidisciplinary effort of at least two different researchers
- a minimum preferred project size is € 400,000 and maximum € 1,000,000.
- project researchers should be willing to cooperate with Hyflux CEPAration at pilot production site in Helmond
- project researchers should be willing to cooperate with other universities and research groups, i.e. in the field of synthesis, testing, characterisation, modelling

Beyond the scope of this program are project proposals that typically:

- only concentrate on modelling

Disclaimer:

- However, proposals based on out-of-the-box-thinking and completely new innovative ideas are encouraged as well

5. Unique character of the program

The uniqueness of the program is that R&D, Pilot Production and Technology Commercialization work closely together in one team comprising of a number of university groups as well. The challenge as well as the opportunity is to build and manage one of the largest teams working from research to commercialization and make it into one of the most successful teams all being aware that success is defined both from scientific and commercialization point of view.

The team will link up with national projects in related areas and stimulate coordination where possible. Professors and key persons at Delft, Twente and Eindhoven University of Technology have been visited to shape the initiative and seek their support for the program, set up, topics and approach.

Unique features of the approach of this program:

- Operate as one large team of Universities, Hyflux Inorganic membrane R&D, and Hyflux Technology Commercialisation
- Coordination of the team by Hyflux (viz. Dr Rinse A. Terpstra + assistant)
- Management of project proposals according to usual STW procedures
- Scientific level guided by University Professors
- Fast track approach is stimulated to focus the R&D work
- Entrepreneurial approach by all involved
- All are keen on new IPR and new products
- Excellent students will be offered job opportunities

6. Duration and budget

The proposed duration of the Program is 5 year, the budget is € 3,000,000 and the funding of the budget is 50 % by STW, 50 % by Hyflux. The Universities contributions is additional and implicitly on a pm base by making available infrastructure, use of equipment and professor and staff guidance.

It is proposed to allocate € 50,000 of the total budget for coordinating activities including travelling and sustenance cost for Program Committee members.

7. Program Committee

The Program will be managed by a Program Committee (PC) consisting of four persons, two nominated by Hyflux, two nominated by STW. The members of the PC have skills and expert knowledge appropriate to assess the proposals and have a high level of experience in the field. PC members may invite other advisory members to the PC meetings, although these will not have voting rights. The PC is responsible for the overall directions and management of the Program. PC meeting frequency will be bi-annual unless PC decides differently based on need. Meetings can be held by videoconferencing. Cost for travelling and sustenance of PC members will be funded by the Program Budget. STW shall appoint a Secretary to the PC who shall not have voting rights. The STW secretary will not be funded from the project and is responsible for the execution of the decisions of the PC.

Short list of PC candidates:

- Ms Olivia Lum, CEO Hyflux Int.
- Dr. Rinse A. Terpstra, CEO/CTO Hyflux CEPAration Technologies (Europe)
- Dr. Anne Julbe, Institut Européen des Membranes, CNRS, Montpellier
- Prof. Dr Jürgen Caro, University Hannover, Institute für Physikalische Chemie und Elektrochemie

For each PC member an assistant will be appointed who can take the place and role of the PC member in case of illness, absence etc.

8. Special conditions for applicants

Universities and Institutions that qualify for STW criteria can apply. A list with special conditions for the university applicants are part of the call for pre-proposals.