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# Atomic Layer Deposition for Membranes: Basics, Challenges and Opportunities

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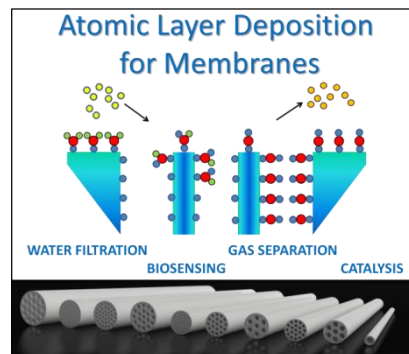
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## **Abstract**

Atomic layer deposition (ALD) is a technology offering the possibility to prepare thin films of high quality materials on high aspect ratio substrates with precise thickness control, high uniformity and excellent conformality, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of synthetic membranes. ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated supports to porous polymers. This minireview aims to provide an extensive summary of the advances of ALD applied to membranes. A selected list of studies will be used to illustrate how the ALD route can be implemented to improve the operational performance of different inorganic, organic, hybrid or composite membranes. Furthermore, the challenges and opportunities of the route for this specific membrane application are also discussed. This work comprehensively shows the benefits of ALD and its application in various facets of membranes and membrane associated engineering processes, and will help exploiting the numerous prospects of this emerging and growing field.

## ToC



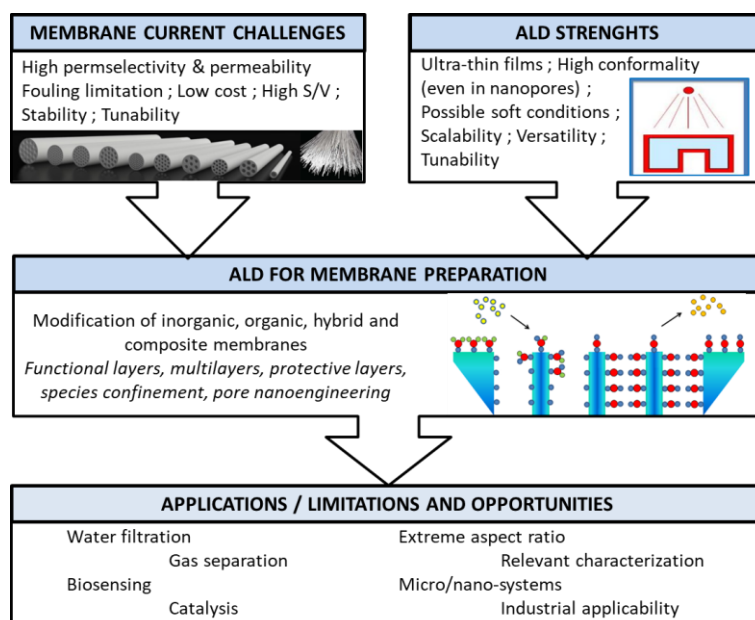
## 1. Introduction

The reduction of pollution and the availability of clean water represent immense challenges for humanity. In industry, chemists classically use processes such as distillation in order to separate the components of large quantities of chemical mixtures into pure or purer forms. These processes are typically very energy consuming, and methods to purify chemicals that are more energy efficient such as membranes could, if applied to the US petroleum, chemical and paper manufacturing sectors alone, save 100 million tons of CO<sub>2</sub> emissions.<sup>1</sup> In this context, the design of highly efficient membranes represents an unexpected resource to considerably reduce costs and environmental impacts of many industries. Membranes can be defined as physical barriers allowing selective transport of mass species. They have become widely used in many separation systems for gas or liquid purification and extraction, water treatment and desalination, catalytic reactors, and various environmental/recycling applications. They also play an essential role in various systems, such as batteries, sensors, fuel cells, electrolyzers and barrier layers.<sup>2-6</sup>

Improvements in nanomanufacturing processes permit now to successfully produce membranes with controllable pores at the nanoscale, which is extremely attractive for their rational design. The ideal nanomanufacturing route should bring control over pore size and distribution, imparting the membrane with high selectivity and permeability, and permit large areas of fabrication to ensure upscaling feasibility. Typically, top-down processes (based on lithography, track etching) bring excellent control on materials nanostructures but are expensive, whereas bottom-up processes (anodization, self-organizing polymerization) present a trade-off for the precise control of pores structure, but are considerably cheaper, opening prospects for the production of low cost and large area membranes.<sup>7</sup>

An upcoming nanomanufacturing tool is Atomic Layer Deposition (ALD), which also represents a promising new route for producing membranes with controlled characteristics at the nanoscale. ALD allows for the preparation of ultrathin films with a sub-nanometer thickness control and excellent

step coverage, even on challenging structures presenting large aspect ratios.<sup>8,9</sup> As the precise control of both the chemical and physical nature of membrane pore surface is a key challenge for membrane producers, the ALD route recently appeared as extremely valuable for membrane science. ALD can be advantageously applied to the area of membranes by fine-tuning their surface properties and hence modifying the interfacial properties, and by controlling the diameter and the aspect ratio of the pores with (sub)nanometer precision. Although ALD has been already applied by many authors to tune membranes properties, only few reports on the synthetic nanopores processing by ALD have been published,<sup>10–13</sup> and to the best of our knowledge, an overview of the subject is still lacking in the literature. Therefore, this review aims to fill this gap. Based on a wide literature data survey, the application of ALD for inorganic, organic, hybrid or composite membranes will be described and illustrated using relevant examples, and the main challenges and opportunities of the ALD route will be assessed. Figure 1 is a representation of the general direction and structure of this overview. It is expected that reviewing all the merits offered by ALD will further increase the interest of membrane scientists and manufacturers such that the method will find its practical use for contributing to extend the range of membrane applications.



**Figure 1:** Representation of the general direction and structure of this overview.

## 2. Membranes and current challenges :

Efficient chemical separations rely on the availability of reliable multifunctional membrane materials with well-defined properties at the nanoscale. For most applications, membrane economics are closely linked to their transport properties: permeability, which determines separation productivity; and selectivity, which determines separation efficiency. An ideal membrane is usually highly selective and very permeable, but a trade-off between permeability and selectivity always exists.<sup>14</sup> To overcome the inherent trade-off relationship between permeability and selectivity, a rational design of membrane materials and membrane processes must combine the selection of the most suitable solids (fluid-solid surface interactions), the optimal membrane microstructure (pore size, porous volume, pore distribution, connectivity and tortuosity), as well as the membrane design (surface to volume ratio, hydrodynamics) and the overall membrane module device. In fact, reactive and non-reactive chemical phenomena occurring at the solid-fluid interfaces play a key role in membrane performance including its permeability and permselectivity (preferential permeation of a component in comparison with another one, often defined as the permeability ratio of the single components) as previously mentioned, but also durability (fouling prevention and long term stability).

The separation and purification processes are achieved by enabling species/molecules to pass through the membrane as a result of a driving force. Most transport processes take place because of a difference in chemical potential (pressure and concentration contribute to the chemical potential).<sup>4-6,15</sup>

Membranes can be manufactured with either symmetric or asymmetric structures, and with different configurations (flat sheets, tubes, honeycombs, hollow fibers...).<sup>5</sup> Porous membranes can be classified according to the size of their pores, as recommended by IUPAC (Table 1).<sup>16</sup> Different pore sizes are suitable for the separation of various types of species/molecules in specific membrane applications. For example, macropores enable the filtration of oil emulsions and bacteria, mesopores

separate most of the viruses, and micropores can be used to separate antibiotics, ions and small neutral molecules (in either gas or liquid phase). Micropores can be further divided in supermicropores (pores size  $> 7 \text{ \AA}$ ) and ultramicropores (pores size  $< 7 \text{ \AA}$ ). Supermicropores are typically used for nanofiltration (NF) whereas ultramicropores can be applied in pervaporation (PV), vapor permeation (VP) and gas separation (GS).

**Table 1:** Membrane classification by pore type, according to IUPAC.<sup>16</sup>

Pore type	Pore size (nm)	Typical membrane applications
Macropores	$>50$	Microfiltration (MF), Ultrafiltration (UF)
Mesopores	2-50	Ultrafiltration (UF)
Micropores	$<2$	Nanofiltration (NF), pervaporation (PV), vapor permeation (VP), gas separation (GS)

Synthetic membranes can be made from a wide range of inorganic, organic, and composite materials structures, and different factors parameters must be considered for the fabrication of effective membranes: obviously the membrane material properties, but also the large scale processability, the module configuration, and low operating conditions. As the effectiveness of a membrane largely depends on its pores structure and surface physical/chemical properties, strong research efforts have been devoted to achieve the optimal materials.

Conventional commercial ceramic membranes are typically based on ceramic oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , or  $\text{ZrO}_2$ .<sup>2-4,6,17-19</sup> In industry, the main manufacturing techniques to produce these membranes are based on powders sintering,<sup>20,21</sup> sol-gel process,<sup>22-24</sup> or (electro)chemical etching processes.<sup>25-27</sup>

Many other inorganic membranes are under development in industry or have been developed at smaller scale for niche applications, based on metals (Pd-based membranes)<sup>28</sup>, perovskites<sup>29</sup>, zeolites (e.g. LTA),<sup>30</sup> silica-based materials (e.g. Vycor® glass),<sup>31</sup> carbons,<sup>32</sup> and silicon carbide.<sup>33-36</sup> Metal-based membranes are generally deposited onto porous (ceramic or metal) supports<sup>37,38</sup> by electroless plating, physical sputtering, chemical vapor deposition (CVD) or magnetron sputtering.<sup>39</sup>

Industrial zeolites membranes are usually grown on porous ceramic supports by hydro/solvothermal methods,<sup>40,41</sup> Vycor® glass is obtained by spinodal decomposition and chemical etching,<sup>42</sup> carbon membranes are obtained by controlled pyrolysis of polymers<sup>43</sup> and commercial SiC membranes are usually obtained by recrystallization methods.<sup>44</sup>

Conventional porous inorganic membranes have generally an asymmetric structure. Indeed, a thin ceramic film of a few microns or less is mechanically very weak and cannot be self-supported. The selective layer is usually deposited on top of a mechanically strong porous support. Intermediate layers are often required between the separative layer and the macroporous support. With their excellent thermal and chemical stability, mechanical robustness as well as their reusability and potential (photo)catalytic activity, ceramic materials are suitable for a wide range of liquid or gas phase membrane processes, even in harsh conditions.

The low cost and wide commercial use of polymeric membranes explains that a large number of polymeric materials have been investigated and reported in the literature. Polymeric membranes are widely used for liquid separation (e.g. water filtration) and number of challenges related to their surface properties (e.g. hydrophilicity, anti-fouling properties) and long term performance are of strong interest for industry. Cellulose acetate is employed for water filtration since the 1950's, and is still used today to fabricate membranes for microfiltration as well as reverse osmosis.<sup>45–47</sup> Many other types of polymers are employed for membrane preparation, such as polysulfones, polycarbonates, polyvinylidene fluorides, polyether, polyethylene terephthalate, poly(dimethylsiloxane), polystyrene, and polyimides, to give a few examples.<sup>15,48,49</sup>

Conventional polymeric ultrafiltration membranes are typically fabricated by solvent casting, forming asymmetric membrane structures.<sup>4,50</sup> In fact, a major advancement in membrane science was the creation of polymeric thin film composite (TFC) membranes, which basically consist of an ultra-thin selective layer (often polymerized) on top of a porous polymeric membrane (interfacial polymerization).<sup>51</sup> Polyamide chemistries are often employed for the selective layer, whereas the porous supports may be prepared from polysulfone or polyacrylonitrile, among others. Mainstream



approaches based on interfacial polymerization are currently used to produce commercial polymeric membranes, due to their easy processing and economic feasibility. Nevertheless, the efficiency of these membranes is hindered by the trade-off effect between permeability and selectivity, and their limited thermal stability.

Figure 2 shows scanning electron microscopy (SEM) images of conventional asymmetric membranes, based on ceramic (alumina) and polymeric (polyvinylidene fluoride (PVDF)) materials, where the average pore size of the support, of the intermediate layers and of the separative top-layer vary from a few microns to a few nanometers.

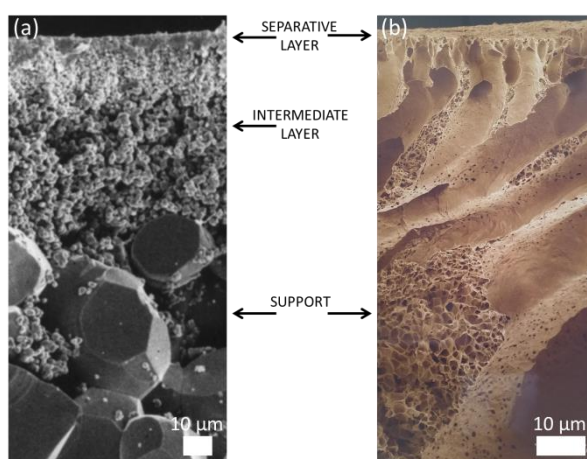


Figure 2: SEM cross-section of (a) a ceramic alumina membrane (Pall), and (b) a polymeric membrane based on polyvinylidene fluoride (PVDF). Both membranes present an asymmetric porous structure and can be used for ultrafiltration (UF) purposes.

Although a large quantity of intercrystalline defects are often present in industrial LTA zeolite membranes used for pervaporation applications, high quality molecular sieve membranes are strongly required for gas separation applications. In order to ensure high separation factors, the mesh sizes of molecular sieve membranes have to be finely calibrated, in the Å range, to allow only the smallest molecules to be transported.

Recent advances in solid state science and nanotechnology pave the way towards the precise design of membranes with controlled properties at the nanometer-scale, in order to obtain both high selectivity and high permeate flux, but also long term stability, controlled surface reactivity and specific functionalities. Of course, the novel membranes manufacturing technologies should be scalable and allow for the control of pore diameter and pore structure in complex materials with relevant mechanical, chemical and thermal stability, in line with the focused application requirements.

A large number of investigations have been made in the past on amorphous Si-based molecular sieve membranes for gas separation and namely H<sub>2</sub> extraction. In order to improve the steam sensitivity of pure amorphous silica, various additives have been inserted in the silica network, such as metals (Ni-SiO<sub>2</sub>,<sup>52</sup> Co-SiO<sub>2</sub>)<sup>53,54</sup> organics,<sup>55</sup> carbon<sup>56</sup> or other oxides.<sup>57</sup> Amorphous oxycarbide,<sup>58,59</sup> oxynitride,<sup>60</sup> or silicon carbide<sup>61</sup> membranes have also been developed, providing thermally activated transport for small gas molecules such as He or H<sub>2</sub>. Silica-based membranes are classically prepared by the sol-gel process or by CVD-based methods. Oxycarbide, carbo-nitride and silicon carbide membranes can be obtained by CVD<sup>59,61,62</sup> or calcination of silicon-based polymers (polymer derived ceramics method).<sup>63–65</sup>

The implementation of ordered or crystalline nanomaterials with controllable micro/mesopores and nanochannels in membranes - such as metal organic frameworks (MOFs),<sup>66–68</sup> zeolites,<sup>69</sup> carbon molecular sieves (CMS),<sup>70,71</sup> carbon nanotubes (CNTs)<sup>72,73</sup> or 2D materials (graphene and graphene oxide, BN, MoS<sub>2</sub>)<sup>74–76</sup> - is gaining a lot of attention because of their high potential for molecular separations, but their use is hindered because of integration challenges at industrial scale. Nanostructured layers made of hybrid materials (MOFs, COFs) or zeolites are often grown on top of porous ceramic membranes by hydro/solvothermal processes<sup>77,78</sup> whereas 1D and 2D materials can be fabricated by CVD and used encapsulated<sup>73</sup> or as free-standing films.<sup>75,79</sup>

A summary of the main types of membrane materials and associated fabrication methods is reported in Table 2. A wide variety of attractive composite membranes can also be fabricated from the combination of the different types of materials, thus associating their benefits.

Table 2: Classification of membrane materials and examples of fabrication methods.

Type of membrane	Materials	Fabrication methods	Advantages and drawbacks
Inorganic	Ceramics (oxides and non-oxides)	Powder sintering, Recrystallization, Sol-gel,	Good physical and chemical stability / high operation cost  15,18
	Metals (Pd-based) (Carbons)	Electrochemical etching, Sol-gel, (PE)CVD, hydro/solvothermal processes, PDC....	
Organic	Polymers (polyacetate, polycarbonates, polyvinylidene fluorides polyimides...)	Polymerization solvent casting Ion-track etching Phase separation...	Low cost, easy manufacturing / limited stability <sup>80,81</sup>
Hybrid	MOFs, COFs, heteropolysiloxanes,	Sol-gel, CVD, hydro/solvothermal	Better stability than organic membranes, additional Functionalities / integration
	HybSi	processes...	

(PE)CVD: (Plasma Enhanced) Chemical Vapor Deposition, PDC: Polymer Derived Ceramics, MOF:

Metal Organic Frameworks, COF: Covalent Organic Framework

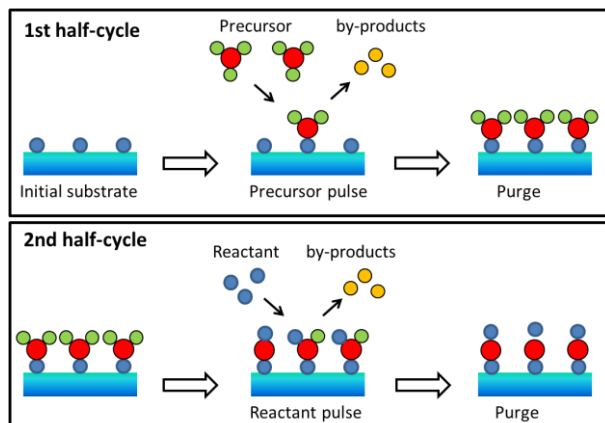
Although considerable advancements have been achieved in membrane science, there are still some critical challenges to tackle. In order to ensure high separation factors with porous membranes, their pores size distribution has to be as narrow as possible, to allow only the selected molecules to cross. In parallel, an easy manufacturing of these pores with controlled sizes, distribution and surface chemistry is a key point for industrial development. In addition to the need for affordable manufacturing processes for compact membrane systems, other important challenges include the limitation of membrane fouling and concentration polarization phenomena as well as the chemical and mechanical stability of membrane elements.<sup>84–88</sup> The latter is essential to ensure their long term use. Concentration polarization is a common and inevitable phenomenon in both pressure driven and osmotically driven membrane processes, and leads to undesirable flux reduction. Membrane fouling is also an important and unavoidable phenomenon in all membrane processes. Lower membrane concentration polarization and fouling processes imply more product, less cleaning and longer membrane life, thereby reducing operational and capital costs. Current strategies to limit concentration polarization and fouling include the adjustment of hydrodynamics, flux management, and the optimization of module design.<sup>84,85,89</sup> The precise tuning of both the chemical and physical nature of membrane pore surface is a thus key challenge for membrane producers and users. ALD, as an enabling technology, can help tackle some of these challenges that membrane scientists are facing when considering industrial applications.

### 3. ALD as a unique and versatile route for the tuning of membranes properties

ALD is a vapor phase deposition technique enabling the synthesis of ultrathin films of inorganic materials with a sub-nanometer thickness control.<sup>8,9</sup> This technology presents unique benefits when compared to other - liquid phase (e.g. impregnation, precipitation, sol-gel) or gas phase (e.g. physical vapor deposition (PVD), CVD) - deposition routes. First, ALD typically allows for the deposition of very pure nanomaterials. When using deposition techniques based on wet chemistry, the removal of potential chemical contaminants can be challenging, especially for depositions on substrates with high-aspect ratio. Another key-benefit of ALD is its high conformality, particularly when compared to other gas phase routes such as PVD. In fact, ALD can be used to coat complex 3D substrates with a conformal and uniform layer of high quality materials, a capability unique amongst thin film deposition techniques.<sup>8,9,90</sup> No other thin film method can even approach the conformality achieved by ALD on high aspect ratio structures. Consequently, ALD-grown materials have a wide range of applications, from biosensing<sup>91</sup> to microelectronics,<sup>92,93</sup> and from nanocatalysts<sup>94</sup> to solar photovoltaics.<sup>95</sup> ALD research began in the 1950s in the former USSR,<sup>96,97</sup> and the technique has been patented in 1977.<sup>97</sup> In the 1990s, the semiconductors industry became interested in ALD<sup>97,98</sup> as the technique emerged as an enabling technology for microelectronic devices fabrication. Since then, the microelectronics industry is the key-driver of the ALD field.

ALD relies on the sequential use of self-terminating gas-solid chemical reactions which sequentially take place in a cycle-wise fashion. A typical ALD cycle consists of alternate pulses of a precursor and reactant gases in the reactor, separated by purge or pumping steps, thus forming two half-cycles. A precursor is typically an inorganic coordination compound, *i.e.*, a metal center surrounded by chemical functional groups called ligands. The -reactant can be, for instance, water or oxygen gas for oxides, nitrogen containing reducing agents for nitrides or true reducing agents (e.g. H<sub>2</sub> gas) for metals. Obviously, each precursor or reactant in an ALD cycle has a profound impact on the process chemistry.<sup>99,100</sup> The conformality benefit of ALD is directly linked to self-saturated chemical surface

reactions, as opposed to other flux controlled techniques such as PVD. The Figure 3 presents a schematic illustration of an ALD cycle.

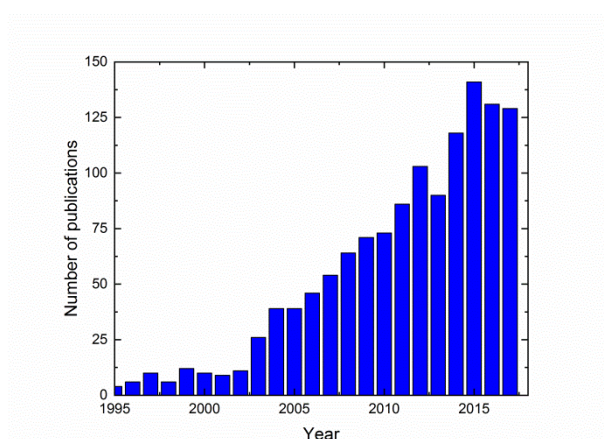


**Figure 3:** Schematic representation of an ALD process cycle. In the first half-cycle, the substrate is exposed to a precursor and then purged. In the second half-cycle, the surface is exposed to a reactant and again purged.

ALD has been used to prepare a wide variety of nanomaterials, oxides, semiconductors and metals, in different morphologies such as thin films<sup>8,9,99,101</sup> and nanoparticles.<sup>102,103</sup> Furthermore, as novel applications of ALD emerged, in areas such as membranes, photovoltaics or flexible electronics, new approaches to integrate new processes, substrates and precursor delivery techniques have been developed (e.g. for temperature sensitive supports). These include energy-enhanced and spatial ALD schemes involving plasma, direct-write, atmospheric pressure, and roll-to-roll processing.<sup>104</sup> For further detailed information about ALD, the reader is referred to excellent recent reviews in this area.<sup>9,92,101,104–107</sup>

Among the methods allowing the preparation of porous membranes with controlled characteristics, ALD has attracted strong attention because of both conformal coating and excellent thickness control at the nanoscale, and because of the wide range of materials that can be deposited. These features

are particularly relevant for the fabrication of size selective membranes, and thus ALD has been used for coating porous membranes since 20 years already. Publications in the area of ALD for membranes considerably expanded in the 2000's decade as revealed by the evolution of the number of publications per year (Figure 4). The application of ALD for membranes is now an upcoming and fast growing field of research.



**Figure 4:** Number of publications per year in the area of ALD applied to membranes, between 1995 and 2017. Data collected from Web of Science using the search terms “atomic layer deposition” & “membranes”.

When a conformal coating of narrow pores is desired, the deposition process should permit to coat membrane porous structures presenting extremely high aspect ratios. ALD is the technique of choice for this purpose. In fact, the self-limiting nature of the reactions taking place in ALD allows excellent step coverage while controlling the film thickness, even on challenging 3D structures with high aspect ratios such as nanopores. To reach a perfect and complete coverage of nanopores, the ALD process parameters have to be optimized. For this purpose, experimental and theoretical work has been carried out to understand how ALD works into high-aspect-ratio structures.<sup>108–112</sup> Using standard ALD processing conditions, the precursor vapor penetrates into microscopic holes through molecular flow.<sup>112–114</sup> When considering ALD in pores at the nanoscale, the process is governed by the so-called Knudsen diffusion mechanism meaning that gas-phase collisions between molecules can be ignored.

Indeed, gas molecules collide with the pore walls more frequently than with each other's ; it occurs when the scale length of a system (here the pore size) is comparable to or smaller than the mean free path of the involved molecules. The diffusion processes have been modeled using Monte Carlo methods.<sup>110,115,116</sup> Furthermore, Gordon *et al.* proposed a mathematical model based on the kinetic gas theory to predict the required precursor exposure time to conformally coat a hole with a defined aspect ratio.<sup>109</sup> This model has been completed by Dendooven *et al.* in order to consider the precursor sticking probability and thus reach more realistic conditions.<sup>110</sup> In a recent review, Detavernier *et al.* extensively illustrated how ALD can be used for the challenging tailoring of nanoporous materials, and the reader is advised to read this beautiful work for more information.<sup>112</sup>

#### 4. ALD for porous membrane preparation or modification

The ALD coatings have been applied on a wide variety of membrane substrates, from inorganic ceramic templated substrates to porous polymers. Whereas most of the reported studies aim to modify the surface physico-chemical properties of the pores (hydrophilicity, organophilicity, catalytic activity...) and to reduce their diameter, others are devoted to the preparation of separative layers with controllable properties.

To the best of our knowledge, the earliest work reporting about ALD on porous membranes was conducted by Kim and Gavallas in 1995, who prepared H<sub>2</sub> selective silica membranes by coating a mesoporous Vycor glass tubular substrate with a thin SiO<sub>2</sub> film, by alternating SiCl<sub>4</sub> and H<sub>2</sub>O vapour reactants deposition (up to 35 cycles). This first gas permeance study through ALD modified membranes showed that their H<sub>2</sub> permeance decreased by about 20%, whereas their selectivity reached values higher than 2000 (at 600°C).<sup>117</sup> The first conformality study within porous membranes was carried out by Dücsö *et al.* in 1996, who reported the deposition of conformal ALD SnO<sub>2</sub> coatings into the 65 nm wide pores of porous silicon with an aspect ratio (AR) of 1:140.<sup>118</sup> The same year, Ott *et al.* also used ALD to coat the pores of porous ceramic alumina membranes (Anodisc®, commercial



membranes based Anodic Aluminum Oxide - AAO) with  $\text{Al}_2\text{O}_3$  films. The liquid-liquid displacement porosimetry method was used to demonstrate that the pore diameters decreased quite linearly with the number of ALD cycles at a rate of  $\sim 0.9 \text{ \AA/cycle}$ , which is consistent with a growth rate on the pore surface of  $\sim 0.45 \text{ \AA/cycle}$ .<sup>119</sup> Since then, a huge amount of studies have been carried out. They are listed in the Tables 3-5 in the following sections dedicated to inorganic, organic and hybrid/composite materials, respectively.

#### 4.1 ALD for porous inorganic membranes

The Table 3 gathers series of research works for the deposition of various types of ALD films on/in porous oxide membrane structures. Please note that the supports on which ALD has been carried often correspond to porous films/structures, and that only few of them were tested as separative membranes. However, we believe that it is important and relevant to report the preparation of ALD films in porous structures aimed to membrane applications, whether they were actually tested or not for separations. Given the large number of studies reported in the literature, this list is non-exhaustive.

**Table 3:** Studies carried out for the preparation of ALD films on/in porous ceramic oxide membranes.

Material deposited by ALD	Reactants of the ALD Process	Ceramic membrane (substrate)	Comments	Application	Reference
			First reported		
$\text{SiO}_2$	$\text{SiCl}_4/\text{H}_2\text{O}$	Silica (vycor) glass	testings of ALD coated membrane	Gas separation	117

SnO <sub>2</sub>	SnCl <sub>4</sub> /H <sub>2</sub> O	Mesoporous silica	First reported conformality study of ALD in nanopores	-	118
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	AAO	First ALD in AAO	-	119
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	MF ZrO <sub>2</sub> membranes	Enhanced permeability and selectivity	Water filtration	11
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	AAO	<i>In-situ</i> gas flux monitoring	-	120
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	AAO	Gas flux measurements	-	121
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	AAO	Gas flux measurements	Catalysis	122
Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	TMA/H <sub>2</sub> O TiCl <sub>4</sub> /H <sub>2</sub> O	AAO	More uniform hydroxylated surfaces	-	123
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	SiO <sub>2</sub>	DNA biosensing	Biosensing	124
SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	TDMAS/H <sub>2</sub> O TMA/H <sub>2</sub> O	Zeolites	Improved catalytic activity	Catalysis	125

			for methane aromatization		
			Final pore size		
SiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O	Mesoporous silica	control near 1 nm	Gas separation	126
			Ion transport study, surface charge modification		
SiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O	AAO		Microfluidics	127
			Reduction of pores size		
SiO <sub>2</sub>	(t-BuO) <sub>2</sub> SiOH/TMA	AAO		Biosensing	128
			Atmospheric pressure ALD, high water permeability		
SiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O	TiO <sub>2</sub> NF membrane		Water filtration	129
			Enhanced mechanical strength		
SiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O	Porous silica diatom exo- skeletons		-	130
			High water permeability		
TiO <sub>2</sub>	TiCl <sub>4</sub> /ethylene glycol	UF TiO <sub>2</sub> membranes		Water filtration	131
			Enhanced dyes		
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	UF TiO <sub>2</sub>		Water	132

		membranes	rejection from water	filtration	
			Strong protein		
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	AAO	adsorption	Biosensing	133
			Enhanced		
TiO <sub>2</sub>	TTIP/ H <sub>2</sub> O	AAO	electropositive character	-	134
			Photoinduced		
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	AAO	hydrophilicity	Self-cleaning	135
			H <sub>2</sub> gas separation	Gas	
TiO <sub>2</sub>	TiCp*(OMe) <sub>3</sub> /O <sub>2</sub> plasma	γ-Al <sub>2</sub> O <sub>3</sub> membrane		separation	136
			N <sub>2</sub> conductance measurements	Gas	
SiO <sub>2</sub> , TiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O, TiCl <sub>4</sub> /H <sub>2</sub> O	γ-Al <sub>2</sub> O <sub>3</sub> tubular membrane		separation	137
			Demonstrated		
ZnO	DEZ/H <sub>2</sub> O	AAO	antimicrobial activity	Biomedical	138
			Uniformity and conformality study	-	139
			Enhanced		
V <sub>2</sub> O <sub>5</sub>	Vanadyl oxytriisopropoxide/H <sub>2</sub> O <sub>2</sub>	AAO	electrochemical	-	140

stability					
WO <sub>x</sub> , VO <sub>x</sub> , MoO <sub>x</sub> , TiO <sub>2</sub>	See Ref	Mesoporous silica	Enhanced catalytic activity	Catalysis	141
Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , TiO <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , ZnO	See Ref	AAO	Ionic transport measurements	Water filtration	142
BN	BBr <sub>3</sub> /NH <sub>3</sub>	AAO	Surface charge modification	Osmotic Energy	143
ZnO, Pt	DEZ/H <sub>2</sub> O, Pt(MeCp)Me <sub>3</sub> /O <sub>2</sub>	AAO	Antibacterial application	Biomedical	144
Ni, Co	NiCp <sub>2</sub> /H <sub>2</sub> O, CoCp <sub>2</sub> /O <sub>3</sub>	AAO	Improved magnetic properties	Sensing	145
Si(CH <sub>3</sub> ) <sub>3</sub>	HMDS-TMCS/H <sub>2</sub> O	8 nm SiO <sub>2</sub> pores within AAO	Highest reported CO <sub>2</sub> /N <sub>2</sub> and CO <sub>2</sub> /H <sub>2</sub> selectivities	Gas separation	146

TMA : Tri methyl aluminum, AAO : Anodic aluminium oxide, TTIP : Titanium isopropoxide, TDMAS : tris(dimethylamino)silane, DEZ : Di Ethyl Zinc, HMDS : hexamethyldisilazane, TMCS : trimethylchlorosilane.

The Table 3 shows that porous Anodic Aluminum Oxide (AAO) substrates are among the most largely investigated membrane supports for ALD of oxides. This self-organized nanomaterial presents a honeycomb-like structure, consisting of high density arrays of uniform and parallel pores, and is commercially available (e.g. Whatman Anodisc®) with nominal pore sizes of few nanometers to few hundreds of nanometers. In addition, the pore length can be controlled from few tens of nanometers to few hundred micrometers, making the aspect ratio potentially very high for this material. The typical fabrication process of porous AAO is electrochemical oxidation (anodization) of aluminum foils in acid electrolytes. Similar processes can be applied to manufacture other porous oxide structures, such as anodic titanium oxides (ATO) for example. These nanomaterials are therefore appealing scaffolds with highly-aligned, parallel pores and narrow pore diameter distributions, particularly suitable for the investigation of ALD for membrane applications.

ALD of oxides is classically used to enhance the hydrophilicity of the pores surface, and the derived layers are used for different purposes. Romero *et al.* used ALD to prepare SiO<sub>2</sub> films within nanoporous anodic alumina (AAO) membranes, and performed ionic transport measurements. By conformally coating the AAO surface and inner pore walls with a thin SiO<sub>2</sub> layer by means of ALD, which reduces both the membrane pore radii and porosity, they found that it also affected the electric fixed charge on the membranes surface. Interestingly, a direct correlation between the membrane effective fixed charge and the NaCl diffusion coefficient could be established. The coating with a SiO<sub>2</sub> thin layer caused a reduction of 75% in the positive effective fixed charge of the AAO membranes, independently of their pore radii and the increase in counter ion transport.<sup>127</sup> Xiong *et al.* characterized anodic aluminum oxide (AAO) membranes before and after coating the entire surface (including the inside pore walls) of the AAO membranes with either Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> by ALD and showed that they exhibited remarkable thermal stabilities.<sup>123</sup>

Several works have proved that ALD could also be used for the modification of (commercial) inorganic ceramic membranes to upgrade their separation performances, for water filtration or gas separation purposes.

Cameron *et al.* reported the first study using ALD to reduce pore diameters of commercial mesoporous alumina tubular membranes by applying ALD of SiO<sub>2</sub> and TiO<sub>2</sub> films. The N<sub>2</sub> permeance measurements revealed that the SiO<sub>2</sub> and TiO<sub>2</sub> ALD layers progressively reduced the membrane pore diameter from its initial size of 50 Å to molecular dimensions, and that gas transport through micropores is governed both by the pore sizes and by the interactions of the transported species with the material at the pore surface.<sup>137</sup> Later on, Li *et al.* used ceramic ultrafiltration (UF) membranes with an average pore size of 50 nm as substrates, on which Al<sub>2</sub>O<sub>3</sub> was deposited by ALD. The pore size and consequently the water permeability of these ceramic UF membranes were easily tuned by modifying the number of ALD cycles. Typically, by increasing the number of ALD cycles, the water permeability was decreased whereas the retention rate was increased.<sup>11,129,131</sup> Shang *et al.* studied the tuning of ceramic nanofiltration (NF) membranes using ALD of TiO<sub>2</sub>. They successfully narrowed the size of active pores, and obtained a low molecular weight cut-off (MWCO) ranging from 260 to 380 Da while maintaining relatively high water permeability at 11-16 L·m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>.<sup>129</sup> Recently, Chen *et al.* used ALD of TiO<sub>2</sub> to prepare NF membranes by tightening ceramic ultrafiltration (UF) membranes. The water permeability remained as high as 32 L·m<sup>-2</sup>h<sup>-1</sup>bar<sup>-1</sup>. In addition, the deposited membranes were used to remove dyes from water and showed significantly enhanced rejection to negatively charged dyes.<sup>132</sup>

McCool *et al.* coated commercial mesoporous silica membranes with ALD SiO<sub>2</sub> and measured N<sub>2</sub> gas permeance, with the aim to produce defect-free molecular sieve membranes. A mesoporous membrane with a N<sub>2</sub> permeance of  $3.5 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup> had its viscous flow reduced to less than 1% with only a modest N<sub>2</sub> permeance reduction to  $2.8 \times 10^{-7}$  mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>. Gas separation experiments indicated that the pore size was in the transition region between mesopores and micropores. A modest separation factor between CH<sub>4</sub> and H<sub>2</sub> of 8.6 was measured at 473 K for the

modified membrane. In addition, the membrane has also been used to perform the challenging separation of *p*- over *o*-xylene, which increased from 1 to 2.1 after modification by ALD.<sup>126</sup>

Tran *et al.* deposited a TiO<sub>2</sub> layer of ~10 nm thick by ALD on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membranes, and the derived membranes assessment revealed a good balance between H<sub>2</sub> permeance and separation properties. At 450 K, the H<sub>2</sub> permeance was approximately  $12.5 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$  and the separation factor was 5.8 for a H<sub>2</sub>/CO<sub>2</sub> equimolar mixture.<sup>136</sup>

Recently, Fu *et al.* synthesized an ultra-thin enzymatic liquid membrane, using carbonic anhydrase enzymes confined within 8 nm wide silica mesopores within AAO templates. In their membrane fabrication process, ALD was used to conduct 5 cycles of alternating hexamethyldisilazane (HMDS), trimethylchlorosilane (TMCS) and H<sub>2</sub>O exposures to quantitatively replace hydrophilic surface silanol groups with hydrophobic trimethylsilyl groups Si(CH<sub>3</sub>)<sub>3</sub>. Attractive CO<sub>2</sub> separation performance were achieved by this ultra-thin enzymatic liquid membrane, with CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> selectivities as high as 788 and 1500, respectively, and the highest combined flux and selectivity yet reported for ambient condition operation.<sup>146</sup>

As evidenced in Table 3, most of the ALD studies applied to inorganic membranes focused on the deposition of oxides on a variety of porous oxide supports. For example, AAO supports have been successfully coated using ALD with a variety of oxide films including SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> as well as WO<sub>x</sub>, VO<sub>x</sub>, MoO<sub>x</sub>.<sup>10,141,142</sup> However, other materials such as metals (Pt, Ni, Co)<sup>144,145</sup> and nitrides (BN)<sup>143</sup> have also been deposited on/in porous oxide supports for membrane applications.

If typical membranes oxide materials such as mesoporous silica, alumina and microporous zeolites have been coated by ALD,<sup>125,126</sup> biomaterials e.g. biominerals, can also be used for the design of advanced nanostructured membrane materials. For example, the unique hierarchical porous

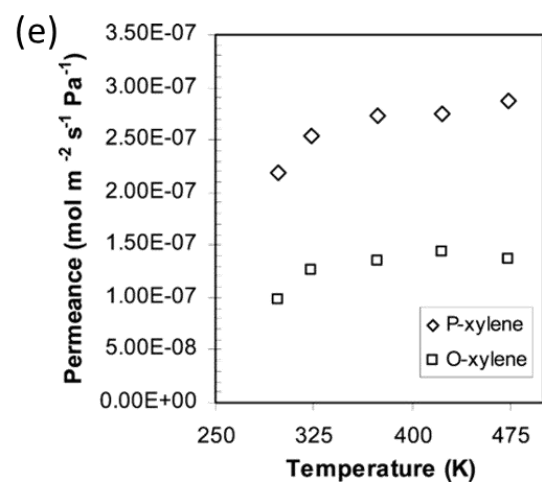
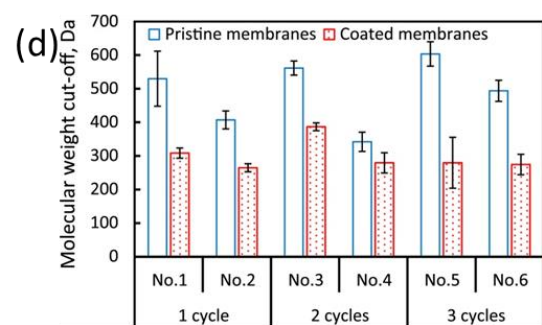
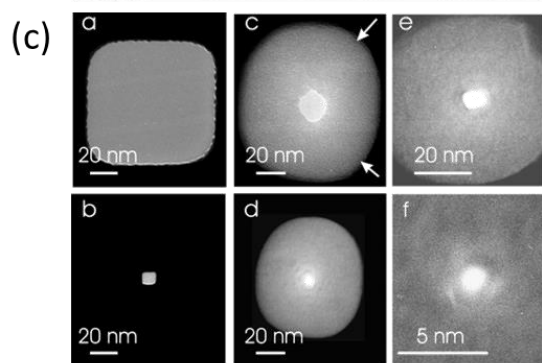
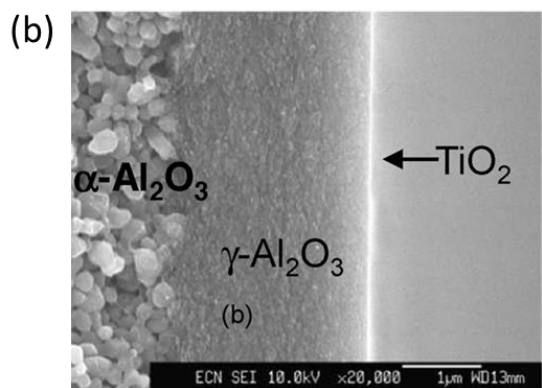
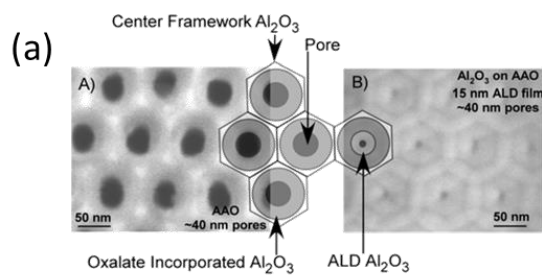


structure synthesized by the unicellular algae called diatoms is particularly attractive for membrane applications. Losic *et al.* modified the pore size of such structures using ALD of  $\text{TiO}_2$ , and found that the mechanical strength and toughness were enhanced by the  $\text{TiO}_2$  coating.<sup>130</sup>

Carbon based materials can also be used as membrane substrates. For example, recently, Feng *et al.* deposited ZnO by ALD on randomly entangled multi-walled carbon nanotubes (CNTs) in the form of fabrics that were directly used as free-standing membranes. The CNT membranes exhibited upgraded water permeability and retention in the ultrafiltration range after ALD.<sup>147</sup>

It is interesting to note that one can as well fabricate nanomembranes with precise pore dimensions by applying micromachining technologies (patterning, lithography, etching) to thin films, enhancing the spectra of (nano)template materials. Fabricated porous templates based on oxides as well as other inorganic materials - e.g. nitrides - have been coated by ALD for membrane applications. Micromachining has been used by Venkatesan *et al.* to fabricate highly sensitive, mechanically robust,  $\text{Al}_2\text{O}_3$  nanopores for DNA detection,<sup>124</sup> and Goerke *et al.* fabricated stable free-standing AlN membranes using focused ion beam patterning and etching on an ALD thin film.<sup>148</sup> In 2004, Chen *et al.* used focused ion beam (FIB) to drill a pore within a  $\text{Si}_3\text{N}_4$  thin film, and then applied 500 cycles of ALD of  $\text{Al}_2\text{O}_3$  to create a nanopore with chosen dimensions, shrinking an oversized pore to a preferred smaller diameter, while keeping its initial shape.<sup>113</sup> Finally, please note that dense membranes can also be fabricated or tuned using ALD. For example, several studies have investigated the growth of yttria stabilized zirconia (YSZ), an ion conducting ceramic, in order to improve its ionic conductivity and reduce the electrolyte film thickness for solid oxide fuel cells applications. For this purpose, ALD supercycles have been used by alternating  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3$  ALD cycles.<sup>149–151</sup>

Figure 5 shows electron microscopy images of different porous inorganic membrane structures coated by ALD, namely AAO (a),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (b) and FIB drilled Si<sub>3</sub>N<sub>4</sub> membranes (c), and illustrates as well the enhanced separation performance of ALD coated membranes (d-e).



**Figure 5:** (a) SEM top view images of an uncoated AAO (left) and a 15 nm ALD alumina-coated (right) membrane showing 10 nm pores remaining. Reprinted with permission from ref<sup>123</sup>, Copyright ACS 2005. (b) Cross-section SEM image of a  $\gamma$ - $\text{Al}_2\text{O}_3$  membrane modified with plasma-enhanced ALD of titania. Reprinted with permission from ref<sup>136</sup>, Copyright Elsevier 2011. (c) TEM images of several pores before (top row) and after (bottom row) deposition of  $\text{Al}_2\text{O}_3$  coatings by ALD. (Left) Even after 500 layers of  $\text{Al}_2\text{O}_3$  coating, a square-shaped FIB pore retains its square shape after its open area is reduced by  $\sim 9$ -fold. (Center) A  $\sim 21.6$  nm diameter ion beam sculpted nanopore was coated with 70 layers of  $\text{Al}_2\text{O}_3$  to produce a  $\sim 4.8$  nm nanopore. (Right) A  $\sim 7.1$  nm diameter ion beam sculpted nanopore was coated with 24 layers of  $\text{Al}_2\text{O}_3$  to produce a  $\sim 2.0$  nm nanopore. Reprinted with permission from ref<sup>113</sup>, Copyright ACS 2004. (d) MWCO separation for different commercial ceramic (titania) nanofiltration membranes coated using 1-3 cycles of ALD of  $\text{TiO}_2$  (red) and non-coated (blue). Reprinted with permission from ref<sup>129</sup>, Copyright Elsevier 2017. (e) p/o-Xylene separation as a function of temperature for commercial mesoporous silica membrane coated with ALD of  $\text{SiO}_2$  (top) and non coated (bottom). Reprinted with permission from ref<sup>126</sup>, Copyright ACS 2004.

#### 4.2 ALD for organic membranes

ALD coatings have been applied to polymeric substrates as well, in order to enhance the performance of organic polymer-based membranes. ALD can be operated at low temperature and is therefore particularly appropriate for efficient modification of common porous polymeric membranes used for liquid separations, including PTFE, PVDF and PP. Indeed, ALD of metal oxide was found to enhance their hydrophilicity and anti-fouling properties, and it was also used to tailor pore sizes. ALD-modified polymer membranes can thus offer higher water permeability and better solute retention properties, which is of high impact for industry.<sup>152,153</sup> A number of research works aiming at the preparation of ALD films on/in polymeric membrane structures is listed in Table 4.

**Table 4 :** Studies carried out for the preparation of ALD films coated on/in polymeric membranes.

<b>Material deposited by ALD</b>	<b>Reactants of the ALD Process</b>	<b>Polymer membrane (substrate)</b>	<b>Comments</b>	<b>Application</b>	<b>Reference</b>
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Porous PTFE membranes	Improved hydrophilicity	Water filtration	154
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Track etched PC	Improved hydrophilicity, resistance to acids and solvents	Water filtration	153
TiO <sub>2</sub> , SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> ,	TTIP/H <sub>2</sub> O SiCl <sub>4</sub> /H <sub>2</sub> O TMA/H <sub>2</sub> O	Track etched PC	Conformality study, ionic transport measurements	-	155
ZnO	DEZ/NO <sub>2</sub>	PVDF MF membranes	Superior water flux of modified membranes	Water filtration	156
TiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> ZnO	TiCl <sub>4</sub> /H <sub>2</sub> O TMA/H <sub>2</sub> O DEZ/H <sub>2</sub> O	PVDF MF membranes	Enhanced anti-fouling	Water filtration	157
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	LLC polymer	H <sub>2</sub> /N <sub>2</sub> selectivity increased from 12 to 65	Gas separation	158
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	HDPE	Barrier layers (tested with He)	Barrier layers	159
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Porous PS–DVB	Enhanced bioactivity	Biomedical	160
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Block copolymers	Membrane template fabrication	-	161

Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	PA membrane	Salt rejection measurements	Water filtration	162
Excellent salt rejection					
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	PES membrane	performance and marginal decrease in the water flux	Water filtration	163
Hydrophilicity and fouling					
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	PVDF membranes	resistance enhanced	Water filtration	164
Gas permeance modified by					
TiO <sub>2</sub>	TiCl <sub>4</sub> /H <sub>2</sub> O	Track-etched PC	ALD film thickness	-	165
Surface changes from					
SiO <sub>2</sub>	SiCl <sub>4</sub> /H <sub>2</sub> O	Track-etched PC membranes	hydrophobic to hydrophilic	Sensing	166
NaCl conductivities					
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Track etched	measurements	Biosensing	167
ZnO	DEZ/H <sub>2</sub> O	PET membranes			
Increased permeability					
TiO <sub>2</sub>	TIP/H <sub>2</sub> O	PP membranes		Water filtration	168
Increased permeance,					
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	PP membranes	fouling resistance enhanced	Water filtration	152
Suppressed thermal					
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	PP membranes	shrinkage	Batteries	169
Improved mechanical					
Al, Ti, and Zn	TMA/H <sub>2</sub> O TTIP/H <sub>2</sub> O	Natural collagen membranes	properties	-	170

DEZ/H <sub>2</sub> O					
Al <sub>2</sub> O <sub>3</sub> ,	TMA/H <sub>2</sub> O	Track etched	NaCl conductivities	DNA	171
ZnO	DEZ/H <sub>2</sub> O	PET membranes	measurements	sequencing	
Al <sub>2</sub> O <sub>3</sub> ,	TMA/H <sub>2</sub> O	Track etched	Reversible nanopore	Biosensing	172
ZnO	DEZ/H <sub>2</sub> O	PET membranes	enclosure		
DEZ/H <sub>2</sub> O					
ZnO	TMA/H <sub>2</sub> O		Increased hydrophilicity,	Water	173
Al <sub>2</sub> O <sub>3</sub>	TTS/ H <sub>2</sub> O	PVDF	Crude oil-	filtration	
TiO <sub>2</sub>	TDMASn/	membranes	resistant membranes		
SnO <sub>2</sub>	H <sub>2</sub> O				

TMA : Tri methyl aluminum, PTFE : polytetrafluoroethylene, PC : polycarbonate, TTIP : Titanium tetraisopropoxide, DEZ : Di ethyl Zinc, PVDF : Polyvinylidene fluoride, LLC : lyotropic liquid crystal, HDPE : high-density polyethylene, PS-DVB : poly(styrene-divinylbenzene), PA : polyamide, PES : polyethersulfone, PET : poly(ethyleneterephthalate), PP : polypropylene, TTC : titanium tetrachloride, TDMASn : tetrakis(dimethylamino) tin(IV)

The Table 4 lists a variety of polymeric membranes which have been modified by ALD. Ion track-etched polymeric membranes have been the most largely investigated substrates. The fabrication of ion track-etched polymeric membranes is based on the irradiation of polymer foils with a defined number of heavy ions whose energy is high enough that the ions completely cross the foils. Then, by selectively dissolving the damaged material, each ion track is converted to an open nanochannel. Ion-track technology is classically applied to polycarbonate (PC), polyethylene terephthalate (PET), and polyimide.<sup>155,174</sup> Polymeric track-etched membranes are commercially available and are very

attractive as templates. The deposited ALD film can be used to control the diameter of track-etched nanochannels, and/or to adjust specific surface properties such as hydrophobicity for example.<sup>155,166</sup> Triani *et al.* and Sobel *et al.* successfully carried out the coating by ALD of high aspect ratio nanochannels in PC track-etched membranes.<sup>165,166</sup> To the best of our knowledge, the work of Triani and coworkers, in which conformal  $\text{TiO}_2$  films were deposited by ALD on PC track-etched membranes, was the first published work using ALD to coat polymeric membranes.<sup>165</sup> The Figure 6a presents the three main steps for the fabrication of these ALD coated track-etched membranes. SEM and TEM images of a conformal ALD coating on/in the track etched polymeric structure are shown in Figure 6b. The Figure 6c shows SEM images of polymeric (PVDF) membranes coated with ALD of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$  and the associate performance enhancement for fouling resistance.

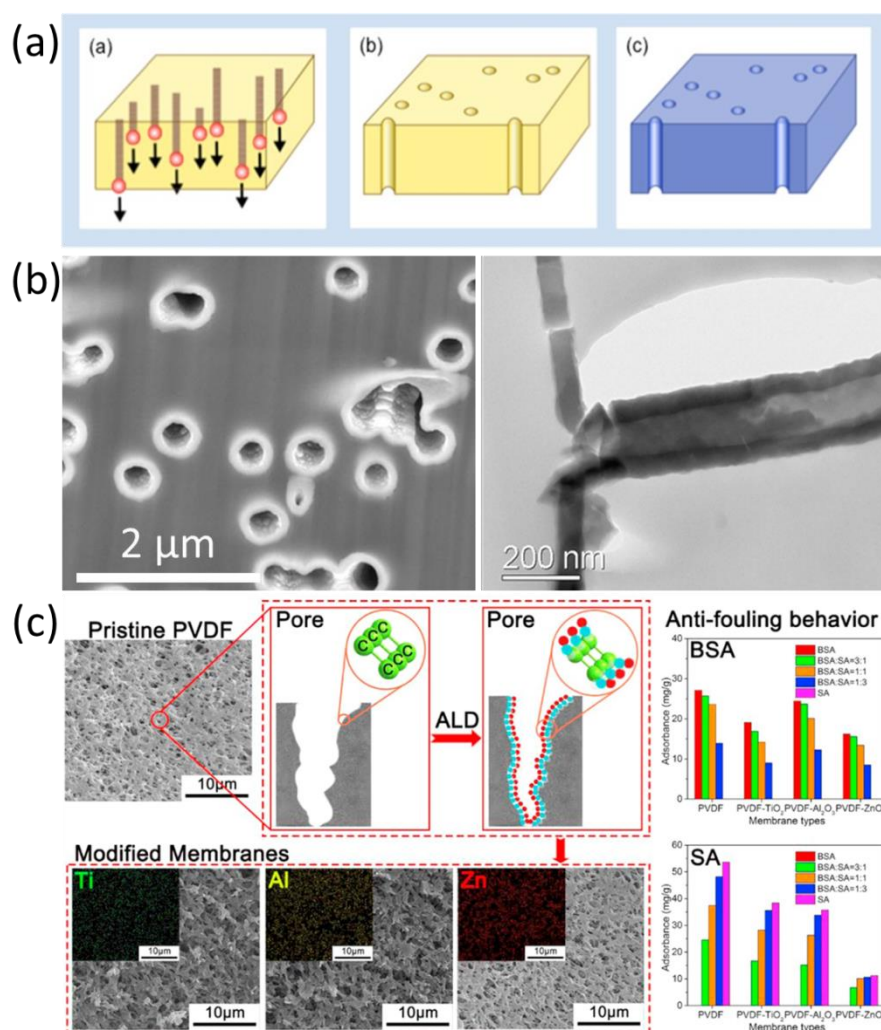




Figure 6: (a) Schematic representation of the fabrication of ion track-etched polymeric membranes: irradiation of PC foil with GeV heavy ions, chemical etching of ion tracks to form cylindrical nanochannels, and ALD conformal coating of the porous membranes. Reprinted with permission from ref<sup>166</sup> (Creative Commons Attribution License 2015). (b) SEM and TEM images of a PC membrane showing 200 nm wide track-etched pores. The ALD TiO<sub>2</sub> conformal coating completely covers the surface and walls of the pore. Reprinted with permission from ref<sup>165</sup>, Copyright RSC 2016. (c) Schematic representation and SEM images of ALD-coated PVDF membranes (left) ; Flux reduction and increase of resistance for a PVDF pristine membrane and ALD modified membranes after adsorptive fouling to bovine serum albumin (BSA) and sodium alginate (SA)(right). Reprinted with permission from ref<sup>157</sup> , Copyright 2018.

Track-etched polymeric membranes coated by ALD were mainly developed for water filtration, but were also investigated for other applications such as gas separation and biosensing.

For example, the first study describing ALD modification of membranes for liquid phase separations has been reported by Li *et al.*, who measured the pure water flux and rejection of a model protein using Al<sub>2</sub>O<sub>3</sub>-modified polycarbonate membranes. The slightly modified membranes (only 10 ALD cycles) yielded strongly enhanced retention rates at the expense of only slight flux loss because of the hydrophilic nature of the deposited alumina layer.<sup>153</sup> Spende *et al.* coated ion-track etched membranes using ALD of different oxides, and tested the ionic transport properties of the ALD-coated nanochannels. Successful conformal coatings of cylindrical 30 µm long nanochannels with initial diameter between 55 and 18 nm were achieved with three different inorganic materials (TiO<sub>2</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>).<sup>155</sup> Abou-Chaaya *et al.* reported the synthesis of uniform biomimetic nanopores with high length (5 µm)/diameter (< 10 nm) ratio, by using both a track-etched technique and ALD. A biological molecule (gramicidin A) was then confined in the nanopores, leading to a better

understanding/control of ion transport mechanisms through nanopores similar to the biological ones.<sup>167</sup>

Gas permeation measurements have also been carried out for modified track etched membranes. Triani *et al.* used ALD to deposit conformal TiO<sub>2</sub> films on/in track-etched polycarbonate (PC) membranes. The flows of N<sub>2</sub> and Ar were measured through the membranes for differential pressures in the range 0–40 kPa. The N<sub>2</sub> permeance at 20 kPa was reduced by ~25% and ~40% for 400 nm thick membranes coated with 250 and 1000 cycles of TiO<sub>2</sub>, respectively. A similar reduction was recorded for the Ar flow through membranes coated with 250 cycles of TiO<sub>2</sub>, confirming ALD as a convenient method for tailoring pore sizes in PC membranes.<sup>165</sup>

Other polymeric substrates were used as well. For example, ALD has been used to modify PVDF, one of the most extensively used membrane materials. The deposition of TiO<sub>2</sub> enhanced both the fouling resistance and hydrophilicity of PVDF membranes, with increasing effect for higher numbers of ALD cycles. In addition, improved water flux and retention were achieved at 120 ALD cycles, as a result of the coupling effect of increased hydrophilicity and reduced pore size.<sup>164</sup> Recently, Li *et al.* compared TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZnO ALD modified PVDF microfiltration membranes by evaluating their anti-fouling properties. It was found that the ZnO modified membrane displayed the lowest adsorption capacity to foulants, the minimum reduction of pure water flux and the smallest increase of membrane hydraulic resistance after fouling.<sup>157</sup> A recent study by Yang *et al.* also reported the preparation of crude-oil-repellent membranes oxide surface engineering enabled by ALD.<sup>173</sup> Recently, ALD of Al<sub>2</sub>O<sub>3</sub> has been firstly demonstrated by Jia *et al.* as an effective method to upgrade the performances of porous polypropylene (PP) hollow fiber membranes. After 50 ALD cycles, the modified hollow fibers membranes showed a 17% increase in water permeance and one-fold increase in BSA rejection. The membranes also exhibited improved fouling-resistance after ALD, and were much more ductile as their elongation at break was increased more than six times after 100 ALD cycles.<sup>152</sup> Alam *et al.* coated polyethersulfone (PES) membranes with ALD TiO<sub>2</sub> films, and showed that the TiO<sub>2</sub> modified-PES membrane exhibited excellent performance with a rejection of ≥90 % for NaCl at room

temperature, which is four times higher than that of a PES membrane alone. Interestingly, the deposition of a 100 nm thick TiO<sub>2</sub> film only resulted in a marginal decrease in the water flux from  $60 \pm 2 \text{ Lm}^{-2} \text{ h}^{-1}$  to  $47 \pm 2 \text{ Lm}^{-2} \text{ h}^{-1}$  of the resulting membrane due to the TiO<sub>2</sub> thin film. Furthermore, the ALD of the TiO<sub>2</sub> film enhanced the membrane mechanical resistance.<sup>163</sup>

ALD has also been applied to infiltrate metals (Ti, Al, and Zn) into natural collagen membranes, which induced crystallographic changes of the collagen likely related to interchain hydrogen bonds and led to improved mechanical stability of the membrane.<sup>170</sup>

Nikkola *et al.* coated polyamide (PA) membranes using ALD of Al<sub>2</sub>O<sub>3</sub>. They showed that the ALD processing parameters had strong influence on both membrane properties and performance. They observed that the most hydrophilic surface was obtained with 10 and 50 ALD cycles at a temperature of 70 °C and 10 ALD cycles at 100 °C. Even an ultrathin ALD coating modified the surface properties of the RO membrane, by increasing both their hydrophilicity and polarity, as well as lowering the surface roughness. These properties are essential improvements for membranes, especially for improving permeability and anti-fouling property.<sup>162</sup>

It has to be noted that ALD on polymers often involves a subsurface component, where some ALD precursors can penetrate into the polymer material, causing modifications of the polymer properties. It is well recognized that ALD on many polymers involves subsurface precursor diffusion and reactions which are not encountered during ALD on solid surfaces. For example, it has been reported that the TMA precursor used for ALD of Al<sub>2</sub>O<sub>3</sub> forms adducts with Lewis base sites within polymers, and the involved reactions are driven by the neighboring bond structure. Therefore, improved understanding and control of specific precursor/polymer reaction pathways is of great impact to maximize the performance of conformal inorganic thin films on polymeric membranes.<sup>175,176</sup>

### 4.3 ALD for hybrid and composite membranes

Membranes can also be based on hybrid (e.g. MOFs) or composite nanostructured materials, and a large number of research groups worked on the synthesis of ALD films within these types of membranes, as listed in Table 5.

**Table 5** : Examples of studies aiming at the preparation of ALD films within membranes based on hybrid nanostructures (MOFs) and composite materials.

Material deposited by ALD	Reactants of the ALD Process	membrane (substrate)	Comments	Application	Reference
Al	TMA	MOFs	MOFs metalation	Catalysis, separation	177
Cu, Ni, Co	ZnEt <sub>2</sub>	MOFs	ALD in MOFs, transmetalation	Catalysis	178
Pt	MeCpPtMe <sub>3</sub>	MOF MIL-101	ALD in MOFs	Catalysis	179
Pt	MeCpPtMe <sub>3</sub>	MOF MIL-101	ALD in MOFs	Direct TEM imaging	180
Co <sub>9</sub> S <sub>8</sub>	Co(amd) <sub>2</sub> / H <sub>2</sub> S	MOFs	MOFs functionalization	Catalysis	181
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Polymer fibers/MOFs		Gas separation	182

Enhanced MOFs nucleation					
ZnO	DEZ/O <sub>2</sub> plasma	MOFs	Conformal films of MOF (ZIF-8)	Microelectronic	183
TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , ZnO	TTIP/H <sub>2</sub> O TMA/H <sub>2</sub> O DEZ/H <sub>2</sub> O	PP/MOFs	Enhanced MOFs nucleation	Filtration, gas storage	184
TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , ZnO	TIP/H <sub>2</sub> O TMA/H <sub>2</sub> O DEZ/H <sub>2</sub> O	Polymer fibers/MOFs	MOFs nucleation	Catalysis	185
ZnO	DEZ/H <sub>2</sub> O	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> membrane/MOF	MOF nucleation, gas separation measurements	Gas separation	186
MOF(-5)	ZnAc <sub>2</sub> / 1,4-BDC	Si/MOFs	MOF synthesis	-	187
Re <sub>x</sub> Al <sub>y</sub> O <sub>3x</sub>	ReO <sub>3</sub> Me/TMA	MOFs	MOFs metalation	Catalysis	188
MOF	Cu(thd) <sub>2</sub> /terephthalic acid	Si/MOFs	MOF synthesis	-	189
Al <sub>2</sub> O <sub>3</sub>	TMA/H <sub>2</sub> O	Porous silver/carbonate matrix	High flux densities of CO <sub>2</sub> and O <sub>2</sub>	CO <sub>2</sub> capture	190
ZrO <sub>2</sub>	TDMAZr/H <sub>2</sub> O	Porous	High	CO <sub>2</sub> capture	191

		silver/carbonate matrix	temperature stability		
ZnO	DEZ/H <sub>2</sub> O	Polyamine/ Polypiperazine thin-film composite	Increased permeability, negative rejection of nitrate ions	Waste water treatment	192
Silanol groups	silsesquioxane (RO) <sub>3</sub> Si-R'-Si(OR) <sub>3</sub> / O <sub>2</sub> plasma	Composite organic/inorganic nanopores	Measurements of He, N <sub>2</sub> , and SF <sub>6</sub> permeances	Sealing layer	193

DEZ: Di ethyl zinc, TMA: Tri methyl aluminum, TDMAZr: Tetrakis(dimethylamido)zirconium(IV), MOFs: Metal Organic Frameworks, TTIP: Titanium tetraisopropoxide.

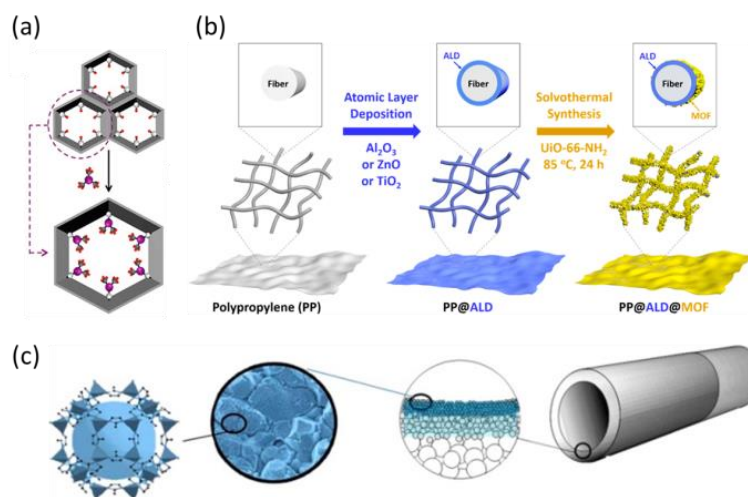
Although the application of ALD for the functionalization of hybrid and composite membranes is still limited, it has been achieved as well, and these ALD coated membranes were also tested for both water and gas phase membrane applications.

Metal-organic frameworks (MOFs) are hybrid porous crystalline materials in which inorganic metal clusters are coordinatively connected by organic linkers. These hybrid materials often provide selective adsorption/transport properties through their micropores.<sup>68,194</sup> Moreover, by combining them with other suitable materials, the properties of MOFs can be further improved for enhanced selectivity, functionality, and stability.<sup>195</sup> MOFs consequently gathered attention as membrane nanomaterials, especially for gas separation applications. However, it is often difficult both to process these materials into reliable membranes and to functionalize their micropores. In the last

few years, ALD was investigated to address these challenges and to modify MOF membrane materials as well.

For example, Rimoldi *et al.* successfully used ALD to deposit rhenium oxide within a mesoporous zirconium-based MOF (NU-1000). The metalated MOF retained its porosity and crystallinity and was found to be catalytically active for ethene hydrogenation.<sup>188</sup> Mondloch *et al.* used TMA precursor pulses in order to obtain the metallation of MOFs with Al (Figure 7a-b).<sup>177</sup> By combining ALD within MOFs pores and metal exchange approaches, Klet *et al.* exchanged the metal atoms in the nodes of the MOF in order to obtain a dispersion of Cu, Ni, and Co single atoms within MOFs pores.<sup>178</sup> Platinum nanocatalysts have been inserted within the nanocages of MOFs by ALD as well, and applied for the hydrogenation of cyclic and linear olefins.<sup>179,180</sup>

It has also been shown that the use of an ALD coating as a nucleation layer facilitates the solvothermal MOF growth on various materials, including polymer fibers.<sup>182,184</sup> Furthermore, as shown by Salmi *et al.*, continuous MOF thin films can be deposited by coupling both ALD and specific solvothermal crystallization procedures, opening up new applications for MOFs by enabling conformal coating of complex 3D structures.<sup>187</sup> For example, MOF thin films were synthesized on silicon substrates using an ALD process based on Cu(thd)<sub>2</sub> and terephthalic acid,<sup>189</sup> and conformal MOFs (ZIF-8) were also grown on pillars coated with a ZnO nucleation layer.<sup>183</sup> Using ALD of ZnO on the grains of a macroporous ceramic support and their subsequent solvothermal conversion to MOFs (ZIF-8), Drobek *et al.* prepared ZIF-8/ZnO/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocomposite tubular membranes (Figure 7c). These membranes were found to extract H<sub>2</sub> from H<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/CH<sub>4</sub> equimolar gas mixtures with remarkably high separation factors.<sup>186,196</sup>



**Figure 7:** Schematic representations of (a) the metallation by ALD in a MOF. Reprinted with permission from ref<sup>177</sup>, Copyright ACS 2013 , (b) the synthetic procedure for integrating UiO-66-NH<sub>2</sub> MOF onto ALD-treated polymeric fibrous scaffolds. Reprinted with permission from ref<sup>185</sup>, Copyright ACS 2017, and (c) the MOF-ZIF-8/ZnO/α-Al<sub>2</sub>O<sub>3</sub> nanocomposite membrane prepared using ALD of ZnO and solvothermal conversion. Reprinted with permission from ref<sup>186</sup>, Copyright Elsevier 2015.

Tong *et al.* fabricated an efficient electrochemical carbon capture composite membrane consisting of carbonate and silver phases, which exhibited a remarkably high O<sub>2</sub> permeation rate after ALD of Al<sub>2</sub>O<sub>3</sub> was used to functionalize the silver phase.<sup>190</sup> Zhang *et al.* deposited a ZrO<sub>2</sub> top-coat by ALD on a porous silver carbonate composite membrane, and showed that the top-layer enabled for an enhanced thermal stability while its pore size was sufficient for the CO<sub>2</sub> molecules to cross.<sup>191,197</sup>

Weber *et al.* and Hao *et al.* used ALD of boron nitride (BN) to coat carbon nanofibers and exploited the hydrophobic property of BN for water filtration.<sup>198,199</sup> Juholin *et al.* coated commercial NF polyamine and polypiperazine thin-film composite membranes with ALD of ZnO and observed improved anti-fouling properties, but the ZnO coating had a tendency to wear off from the membrane surface as revealed by the increasing Zn concentration in the permeate stream. This degradation strongly limits the life time and potential use of these coated membranes.<sup>192</sup>



Finally, it has to be noted that Molecular Layer Deposition (MLD) - a technique developed for the layer by layer preparation of nanoscale films of organic materials – has also been applied to tailor membrane surfaces and improve their separation properties. ALD and MLD share many common film growth characteristics, such as the chemistry based on surface-controlled reactions and the conformality of the materials prepared.<sup>200</sup> Xiong *et al.* used MLD for the deposition of polyimide (PI) on the pore walls of polypropylene (PP) membranes, and surface hydrophilicity and improved permeation performance (30%) have been achieved. The overall separation efficiency remains higher than 85% even after 250 MLD cycles.<sup>201</sup> The same group also prepared thin film composite membranes by MLD of PI on nanoporous AAO substrates, and observed that only a few layers led to upgraded retention rate from nearly zero for the neat alumina substrate to ~82% for the coated ones, whereas the water permeability still remained high.<sup>202</sup>

#### 4.4 Summary of results obtained

All the reported examples of ALD films show that the excellent film conformality coupled with the subnanometer film thickness control offered by ALD make this route a powerful tool to finely tune the membrane materials properties, even at large scale. The reported ALD studies mainly focus on the modification of macro-, meso- and microporous membranes, by imparting them with functional nanolayers. These ALD coatings modify the pores surface properties, allowing to improve their mechanical and chemical stability, but also to enhance the performance of membranes (inorganic, organic, hybrid or composite materials) as shown in the numerous examples reported for gas separation, water filtration, biosensing and catalysis.

Few examples illustrating these key applications are summarized hereafter. ALD coatings effectively permit to reduce pores diameters of ceramic membranes and thus improve their gas separation performance, as shown in the examples where ALD of TiO<sub>2</sub> was applied to coat  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membranes and reach higher H<sub>2</sub> gas separation factors,<sup>136</sup> or where mesoporous silica membranes were coated

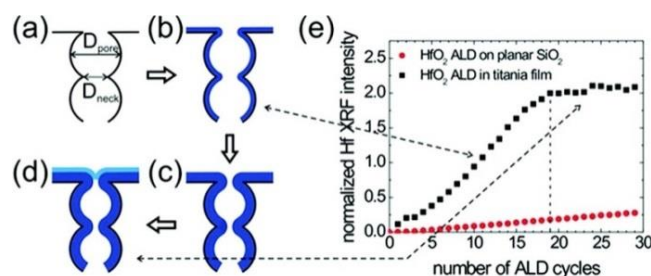
with ALD of SiO<sub>2</sub> to improve p/o-xylene selectivity.<sup>126</sup> Concerning water filtration, one of the most functional behaviour provided by ALD is the enhancement of anti-fouling property, as many studies reported that membranes coated with ALD of oxides offer enhanced retention of pollutants at only slight expense of flux loss because of the hydrophilic nature of the deposited layers.<sup>157,164,173</sup> In addition, the low roughness obtained after ALD coating also helps achieving high liquid permeability.<sup>162</sup> ALD has been applied by many authors to coat polymeric track etched nanopores, in order to reduce pores dimensions and obtain smooth surfaces, allowing for both precise ion transport studies and prospects in biosensing applications.<sup>171,172</sup> Finally, ALD was used to coat porous membranes with functional catalytic nanolayers. For example vanadia-coated AAO membranes prepared by ALD yielded improved selectivity for the catalytic oxidative dehydrogenation of cyclohexane,<sup>122</sup> and metallic nanocatalysts have been inserted within MOFs nanocages by ALD, and applied for catalysis as well, *e.g.* for the hydrogenation of both cyclic and linear olefins.<sup>178,179,181</sup> These few examples effectively demonstrate how the modification of surface properties by ALD affects and enhances the membrane materials performance.

## 5. Limitations and opportunities

To achieve the development of any highly efficient emerging membrane technology, i.e. its industrial application and commercial success, both precise control over device performance and reproducibility coupled to easy scalability of the membrane synthesis process are required. ALD, an enabling and scalable technology, provides a tunable route for modifying the interfacial properties of (nano)pores. This technique has been exploited to tune the properties of a wide variety of membrane materials with unparalleled precision, as shown in the numerous examples reported for gas separation, water filtration, bio-sensing and catalysis. By imparting pores with functional nanolayers, ALD coatings are able to improve the mechanical and chemical stability of membranes, limit fouling phenomena and enhance overall system performance. However, before considering

The first obvious challenge is related to the fact that most mesoporous and microporous membranes present pores with very high aspect-to-surface ratios. In fact, mesoporous or microporous membrane materials such as zeolites or MOFs can present aspect ratios over 10000. Even if ALD allows for extremely conformal coatings, the deposition of films in these nanostructures is extremely challenging. The choice of the precursor and co-reactant chemistries, but also their extended exposure and purge times during the ALD process become crucial, as the pore narrowing may result in less deposition near the bottom of the pores because of diffusional limitations<sup>109,110,112</sup><sup>109,110,112</sup><sup>109,110,112</sup><sup>109,110,112</sup><sup>109,110,112</sup><sup>109,110,112</sup><sup>108,109,111</sup><sup>108,109,111</sup>.<sup>109,110,112</sup>

Furthermore, depending on the shape of the meso/micropores, pore closure can occur after a number of ALD cycles,<sup>203,204</sup> resulting in a decrease of membrane permeance and overall performance. To illustrate this case, Dendooven *et al.* used a porous substrate with ink bottle pores, and coated the mesopores with HfO<sub>2</sub> using ALD.<sup>204</sup> The Hf-uptake per ALD cycle was monitored using *in situ* X-Ray Fluorescence (XRF). The results revealed that pore necks became too narrow after 19 ALD cycles, and were no longer accessible for the Hf-precursor molecules. From then on, ALD continued on top of the coated mesoporous film (Figure 8).



**Figure 8:** (a–d) Schematic representation of conformal ALD of  $\text{HfO}_2$  in titania mesopores. (e) *In situ* XRF during  $\text{HfO}_2$  ALD on either planar  $\text{SiO}_2$  substrate or mesoporous titania film: evolution of Hf  $L\alpha$  (7.9 keV) peak area vs. the number of ALD cycles. As depicted in (d), the pores are no longer accessible for the Hf-precursor molecules and from then on, ALD film grows on top of the coated mesoporous film, as observed in the XRF spectra (e). Reprinted with permission from ref<sup>204</sup>, Copyright ACS 2012.

Another limitation is the fact that the pores in conventional ceramic membranes usually present a certain size distribution, which can be more or less narrow. The ALD parameters thus need to be adapted and optimized to the pore size distribution of the considered membranes supports. Even if the ALD processes can hardly be universal, they remain very versatile.

One further challenge to consider is the fact that ALD coating may wear-off during membrane operation. This has been observed for ZnO coated polymeric membranes,<sup>192</sup> but this issue may be true for other ALD materials as well. Despite the mechanical stability of the coatings, in order to reach a real industrial application, the chemical and mechanical stabilities, as well as the durability of the ALD coatings have to be further investigated in close relation with the selected supports and membrane operation conditions. There is no doubt that the confinement of ALD materials within membrane pores (in comparison with surface top-layers) is a strong asset for limiting the ALD material abrasion upon use, but proving their long term stability in harsh working condition would be a key step.

As introduced earlier, the application of ALD to membranes being an emerging and growing area of research, numerous opportunities have still to be exploited. As evidenced in this report, a large

number of research works have been carried out to enhance/modify the properties/performance of either porous ceramic membrane supports, especially AAO, or those of porous polymeric templated supports, such as track-etched membranes.

Dense membranes could also be further optimized using ALD. This route could attractively be used for surface modification of either dense inorganic membranes such as Pd-alloys or ion-conducting ceramics such as perovskites, whose performance might be limited by either poison compounds (e.g. sulfur) or low surface exchange with the gas phase. Dense YSZ thin films have already been synthesized by ALD to conduct oxygen ions for fuel cells applications. Similarly, ultra-thin films of metallic palladium could be prepared on top of nanoporous membrane supports to generate competitive H<sub>2</sub> permselective membranes. In fact, only a very limited amount of precious metal is required for ALD in comparison with conventional Pd-based membranes. Novel nanocomposites materials (e.g. nanolaminates) could also be developed and tested as dense membranes for H<sub>2</sub> purification. The deposition of ultra-thin conformal layers with relevant microstructure and composition (i.e. blocking poisoning species or increasing specific surface area) could be efficiently operated by ALD. In addition, the membrane composition could be gradually and easily tuned from the support to the top-surface, using ALD super cycles.

Furthermore, only few ALD works were dedicated to composite membranes. ALD is an ideal technique for local addition of materials with atomic scale precision in nanostructures, which could advantageously be applied to such composite membranes. For example, as ALD allows to functionalize nanomaterials surfaces, the technique could be used to enhance the compatibility of inorganic molecular sieve fillers with the polymeric matrix of mixed matrix membranes (MMM). Furthermore, as many ALD processes allow for low temperature deposition, they would be compatible with deposition on/in composite membranes based on a polymeric matrix. The development of novel MLD processes could also be very helpful to address this purpose.

Even in the area of MOFs materials, which gather strong attention from the ALD community, there are still a lot of opportunities that could be exploited. The combination of inorganic ions and organic

molecules in MOFs opens for an almost infinite number of structures, flexibility in pore size, as well as functionalization potential. Thus, the chemistry of ALD precursors could help achieving many more metallations of various types of MOFs. Furthermore, as many chemistries are allowed by ALD, a thin ALD coating of the external MOF surface could enhance their compatibility within MMM. In addition; the possibility to prepare crystalline MOF thin films by ALD have recently emerged, opening novel possibilities of disruptive membrane technologies.<sup>183,189,205</sup> For example, ALD MOFs could be directly grown in pores at the nanoscale.

Catalytic membranes for nanoreactors could also benefit from ALD. The membrane reactor concept, combining in the same unit a conversion effect (catalyst) and a separation effect (membrane), has many potential benefits for a range of chemical reactions.<sup>206</sup> Vanadia-coated AAO membranes prepared by ALD were tested for the catalytic oxidative dehydrogenation of cyclohexane, and showed improved selectivity at the same conversion compared to conventional powdered alumina supported vanadia catalysts.<sup>122</sup> ALD is a relevant tool for the synthesis of catalytic and electrocatalytic materials -oxides, carbon, hybrids, metals, non oxides- and controlled distribution of size, composition, and active site.<sup>207</sup> Numerous opportunities are consequently expected for the development of ALD membranes for catalytic, photocatalytic and electrocatalytic reactors, including also membrane nanoreactors. The slow diffusion of ALD chemical precursors within the Ångstrom sized pores of MOFs and zeolites makes ALD challenging in these structures, but it can be achieved. Indeed, a few studies reported the insertion of NPs within such crystalline materials, e.g. ALD of Pt NPs in MOFs (MIL-101-Cr).<sup>179,180</sup> Many more opportunities will have to be exploited in this area, with MOFs, zeolites or other nanomaterials presenting complex architecture (e.g. hierarchical porous networks). Thermally post-treated ALD films can actually be used as nanomembranes for improving the stability/life-time or even the selectivity of catalysts, opening up new opportunities. For example, Lu *et al.* prepared ALD of Al<sub>2</sub>O<sub>3</sub> overcoats on alumina-supported Pd nanocatalysts and observed the formation of mesopores of ~ 2 nm after high-temperature treatment at 700°C. The pores resulted from structural changes in the amorphous Al<sub>2</sub>O<sub>3</sub> overcoat, and enabled the embedded Pd NPs to be

accessible to reagents. Both high catalytic activity and good thermal stability were offered by these nanomembranes.<sup>197</sup> Zhang *et al.* deposited a ZrO<sub>2</sub> overcoat on a porous silver carbonate matrix membrane, and showed that the overcoating layer enhanced the thermal stability whereas the pore size was sufficient to allow CO<sub>2</sub> transport.<sup>191</sup> Other materials than alumina and zirconia could be prepared by ALD as relevant overcoats to both create specific nanoporosities and increase the thermal stability of sensitive/unstable catalytic systems. The application of ALD for the preparation of nanomembranes-encapsulated catalysts should be also considered for controlling the selective transfer of reactants and/or products to and from the catalytic sites.<sup>208</sup>

Membranes utilizing 1D (e.g. CNTs) and 2D materials (e.g. graphene, MoS<sub>2</sub>, BN) are attractive candidates for membrane applications, especially for molecular separations.<sup>75,76</sup> Very recently, considerable research efforts focused on both ALD coatings on/in 1D and 2D materials,<sup>209–211</sup> as well as on the ALD synthesis of 2D materials.<sup>212–216</sup> As both the use of 2D materials as membranes and the ALD synthesis/coating of 2D materials are barely emerging, there is a real opportunity for breakthrough cross-science innovations by combining these fields of science.

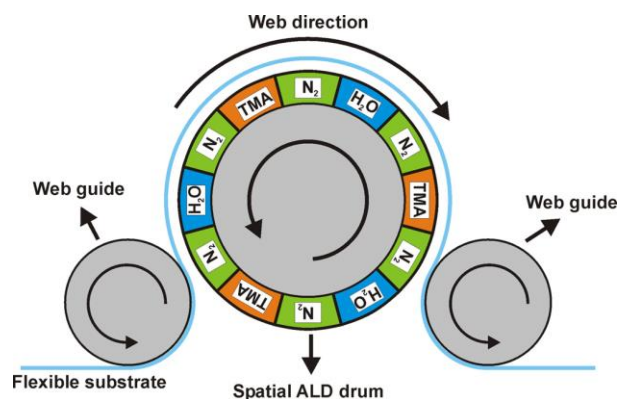
ALD being a very versatile technology, many possibilities can be explored by changing the recipes parameters, in order to obtain the desired effects of surface properties modified by ALD to enhance the membrane performance. Nanolaminates and nanoalloys can be prepared within membrane pores, using ALD supercycles. The possibility to prepare membranes with composition gradients using supercycles is very attractive e.g. for protection layers or diffusion barriers. ALD can also be used to confine nanomaterials - including nanoparticles with controllable dimensions and composition,<sup>102,103</sup> or MOFs<sup>189</sup> – directly within the membrane pores. The possibility of embedding reactive metallic catalysts and choosing their location is very attractive for the nanoreactor community, and other materials (than platinum) could also be introduced within MOFs. In fact; even the infiltration level in the support could be controlled by tuning the ALD process (e.g. using plasmas or short precursor exposures). Also, the recent development of selective ALD processes for

nanopatterning<sup>217</sup> and atomic layer etching (ALE)<sup>218,219</sup> could be explored for the precise tuning (or even reparation) of membranes.

The huge advantages of ALD allow for the functionalization of porous materials as well as for the atomic-level tuning of pore size, and the availability of many commercial ALD reactors makes ALD accessible for researchers in different fields of science, including the membrane community. However, the use of ALD reactors for the production of membranes is still hindered by technical limitations and issues before it can be applied to industrial membrane systems.

The limitations of the route are the complexity and cost of both the deposition reactor and associated metal precursors, which have a strong impact on the popularity of the method for membrane producers. The first issue is the cost of this vacuum based technology. Both capital and operational costs are currently considered as relatively high for membrane production. The second issue is the design of ALD reactors, which are classically shaped for thin films depositions on wafers, as the semiconductor industry is the driver of this technique. However, novel ALD reactor designs are currently being developed in order to increase the deposition throughput and extend ALD applicability, opening up new opportunities. For example, tubular and flow-through reactors have been developed to allow conformal coatings of porous materials on/in conventional tubular ceramic membranes.<sup>220</sup> Furthermore, the recent development of low temperature processes and roll-to-roll ALD reactors (Figure 9),<sup>104,221,222</sup> initially developed for flexible electronic applications, will certainly enable economically viable ALD coatings on polymeric flat-sheet membranes and thus offer real ALD industrial opportunities.





**Figure 9 :** Schematic of a roll-to-roll ALD concept for the deposition of  $\text{Al}_2\text{O}_3$  films on flexible substrates, consisting of a central rotating drum that contains combinations of TMA and water half-reaction zones, separated and surrounded by nitrogen gas bearings. The flexible substrate to be coated is pulled over this drum. ALD deposition takes place when the substrate is moved over the drum. The total thickness of the nanolayer prepared is determined by the rotation frequency of the drum in combination with the movement speed of the foil. This type of reactor is developed at TNO (Netherlands Organisation for applied scientific research). Reprinted with permission from ref<sup>222</sup>, Copyright AVS 2012.

Next, there is also room for improvements on the characterization side. Indeed, there is a need for better understanding on how the modification of surface properties by ALD affects the membrane materials (and performance). For example, as ALD on polymers often involves a subsurface component, where ALD precursors can penetrate and modify the polymer material, better understanding of the specific precursor/polymer reaction pathways are crucial to achieve controllable thin film coatings in the pores of polymeric membranes. The impact of the surface charge of the pores on the membrane permeance is also not well understood yet, and more research efforts are thus required. Although the materials deposited by ALD within pores have been studied using conventional *ex-situ* methods such as electron microscopies (SEM, TEM), or by measuring variations in fluid transport mechanisms through the pores, *in-situ* analysis are also very much desired. The monitoring of the reduction of AAO membrane pore diameters during ALD has been

reported using *in situ* N<sub>2</sub> and Ar permeation measurements,<sup>120</sup> and these measurements demonstrated that mesopores can be reduced to molecular dimensions with atomic layer control under monitoring. *In-situ* fluorescence (XRF) measurements during ALD in/on nanoporous films have also been carried out to control the material added in the pores,<sup>223</sup> but this technique is rather complicated to implement, since it requires a synchrotron light source.

Ellipsometric porosimetry (EP) is a powerful technique to characterize both the porosity and pore size distribution in porous nanostructures, and more specifically in thin layers such as membranes.<sup>57,224–227</sup> The huge potential of *in-situ* EP for monitoring the accessible porosity and pore size after ALD coatings has been demonstrated in the past, e.g. for ALD of TiO<sub>2</sub> in mesoporous silica,<sup>111</sup> but there is still enormous potential to apply this EP technique to other ALD chemistries and other types of porous membrane materials. Furthermore, other *in-situ* characterization techniques such as IR/Raman spectroscopies<sup>228,229</sup> or acoustic emission analysis<sup>230,231</sup> could also be explored to investigate/monitor the ALD gas transport mechanisms and (pores) surface phenomena like adsorption/desorption within the membrane materials.

## 6. Conclusions

The reduction of pollutions, the availability of clean water and the production of affordable and sustainable energy represent immense and pressing challenges for which membrane technologies can play a key role. The ideal manufacturing route for the production of porous membranes should enable a precise control over pore dimension and distribution, be scalable, cost-effective, and have a minimum environmental impact. The surface modification of both porous and dense membranes is also a key strategy to control and optimize the membrane properties and functionalities for specific applications. Recent improvements in nanomanufacturing methods permit now to successfully produce pores through ultra-thin films and to tune solid surface properties, which is extremely

attractive for the rational design of membranes with optimum solid/fluid interactions and performance.

Atomic layer deposition (ALD) is a scalable technique allowing the deposition of high quality materials with high uniformity, precise growth control, and excellent conformality. ALD offers nanoengineering capabilities and a versatility that conventional methods cannot meet. The route is therefore currently used for the most challenging thin-film deposition applications, and opens new possibilities for the precise design of large membrane devices, by imparting them with functional nanolayers.

Since the early work on ALD of  $\text{SiO}_2$  on porous membranes in 1995, many ALD processes have been developed and applied to tune the properties of pores of a wide variety of membrane supports, from inorganic substrates to porous organic polymers. The ALD studies reported were focused on macro, meso and microporous membranes, and a large number of studies where aiming at the preparation of ALD films within ceramic and polymeric membrane structures as well as on novel hybrid and composite membrane materials.

ALD has mainly been used in order to obtain pores with chosen diameters and aspect ratios. Oxide coatings often increased the hydrophilicity of the pores surface, although this was usually not the main purpose. Templated AAO support were selected as model supports for conformality studies of ALD coatings, and numerous examples have been described in this review, where ALD was used to improve the performance of inorganic, organic, hybrid or composite membranes, for either liquid phase or gas phase applications. It appears clear that an impressive number of nanoengineering capabilities offered by ALD are particularly relevant for membranes, as they enable:

- The synthesis of membrane materials with complex designs: The route can be used to tune macro, meso and micropores with high aspect ratios, as well as derived complex porous structure such as

hierarchical porous membranes. The possibility to confine nanomaterials – including nanoparticles or MOFs – directly within pores is also possible.

- The preparation of coatings with tailored compositions and nanostructures: The wide choice of ALD precursors and processes allows the preparation of conformal films of oxides, but also of non-oxides such as nitrides and metals, with various degrees of crystallinity. These nanolayers can bring additional functionalities to the membranes. Nanolaminates and nanoalloys with composition gradients can also be prepared within pores, using ALD supercycles.

- The control over the surface/fluid interactions: the smoothness is enhanced, and depending on the ALD coating applied, the membrane hydrophilicity/organophilicity can be tuned, and the nanomaterials present in/on the pores can affect as well the surface charges and adsorption/antifouling properties.

- The local tuning of functionality: ALD can modify the reactivity and the properties of the pore surface, for examples making them catalytic (electrocatalytic, photocatalytic), and thus enabling the preparation of functional nanoreactors by modifying existing membranes.

This review shows the huge benefits of ALD for the tuning of membranes, such as the atomic-level tuning of pore dimensions and the functionalization of various materials. The ALD-modified membranes have been tested for many applications, including water filtration, gas separation, biosensing and catalysis. With the optimization of ALD chemistries and processes, the advancement of characterization techniques and specific designs of reactors, there are many opportunities yet to be exploited that could enable the manufacturing of membranes with enhanced permeability, selectivity, reactivity or durability, which will, hopefully, rapidly transfer from research labs to industrial scale applications.

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**Abbreviations:**

AAO: anodic aluminum oxide

ALD: atomic layer deposition

ALE: atomic layer etching

AR: aspect ratio

ATO: anodic titanium oxides

BSA: bovine serum albumin

CNTs: carbon nanotubes

CSMs: carbon molecular sieves

CVD: chemical vapor deposition

DEZ: di ethyl zinc

DNA: desoxyribonucleic acid

EP: ellipsometric porosimetry

FIB: focused ion beam

GS: gas separation

HDPE: high-density polyethylene

HMDS: hexamethyldisilazane

IUPAC: international union of pure and applied chemistry

LLC: lyotropic liquid crystal

LTA: linde type A

MF: microfiltration

MLD: molecular layer deposition

MMM: mixed matrix membrane

MOFs: metal organic frameworks

MWCO: molecular weight cut-off

NF: nanofiltration

PA: polyamide

PC: polycarbonate

PECVD: plasma enhanced CVD

PES: polyethersulfone

PET: poly(ethyleneterephthalate)

PP: polypropylene

PS-DVB: poly(styrene-divinylbenzene)

PTFE: polytetrafluoroethylene

PV: pervaporation

PVD: physical vapor deposition

PVDF: polyvinylidene fluoride

RO: reverse osmosis

SA: sodium alginate

SEM: scanning electron microscopy

TDMA: tris(dimethylamino)silane

TDMA<sub>Sn</sub> : tetrakis(dimethylamino) tin(IV)

TDMAZr: tetrakis(dimethylamido)zirconium(IV)

TEM: transmission electron microscopy

TFC: thin film composite

TMA: tri methyl aluminum

TMCS: trimethylchlorosilane

TNO: Netherlands organisation for applied scientific research

TTC: titanium tetrachloride

TTIP: titanium isopropoxide

UF: ultrafiltration

VP: vapor permeation

YSZ: yttria stabilized zirconia

XRF: X-ray fluorescence



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## **Bibliographies**

### **Matthieu Weber**



Dr. Matthieu Weber obtained a double M.Sc. in Material science Engineering and Nanotechnologies in 2009 from the University of Technology of Troyes (UTT), a leading French engineering school. He completed his Master's thesis at the Helmholtz-Zentrum Berlin (Germany), where he worked on the development of ZnO thin films for solar photovoltaics. He then carried out his doctoral research work in the frame of a collaborative European project (Marie Curie Actions), focusing on ALD of noble metal nanoparticles in the Kessels group, and obtained his Ph.D. in 2014 from the Eindhoven University of Technology (The Netherlands). He is currently working as a postdoctoral researcher at the European Institute of Membranes of Montpellier (France), where he focuses his work on the ALD synthesis of nitrides and metals nanomaterials for water filtration and gas separation membranes. His research interests include as well the synthesis of nanostructured membranes and MOFs. He is a member of the Marie Curie Fellows Association (MCFA) and he is also the co-organiser of the yearly French ALD conferences (RAFALD 2017 and 2018).

### **Anne Julbe**



Dr. Anne Julbe obtained her PhD in 1989, for the development of sol-gel derived SiC and SiO<sub>2</sub> membranes and materials. In 1989 she received a tenure researcher position at the CNRS, in the group of Prof. Louis Cot. She initiated an activity on ceramic membranes for gas separation and catalytic reactors, namely with nanophase oxides and zeolites. In 2002 she defended her Habilitation thesis on the "Contribution of Material Science to the development of Membrane reactors" and got the position of CNRS-Directeur de Recherche in 2004. She led a research department on the "Design of Membrane Materials and Multifunctional systems" in the period 2010-2014, and is now leading a team in the area of "Molecules, colloids and porous materials" at the European Institute of Membranes of Montpellier (UMR CNRS 5635). Her current interests include the design and on-line characterisation of original nanostructured multifunctional membranes for applications in gas separations, catalytic reactors, sensors and electrochemical systems.

### **André Ayral**



Prof. Dr. André Ayral received his Ph.D. in "Dense Media and Materials" from the University of Montpellier (France) in 1988. He first served as research engineer at the French Nuclear Agency (CEA). He then joined the Graduate National Higher School of Chemistry of Montpellier (ENSCM) as an assistant professor in 1991. Since 2002 he is Professor of Chemistry at University of

Montpellier. He is currently coordinator of the Erasmus Mundus Master in "Membrane Engineering". He is also Vice-President of the Materials Science French Federation. He carries out his research activities within the European Institute of Membranes of Montpellier. His main research interests include synthesis and characterization of inorganic and hybrid porous materials, thin films, and multifunctional membranes.

#### **Philippe Miele**



Prof. Dr. Philippe Miele received his PhD in Inorganic Chemistry in 1993 from the University of Montpellier. Following a postdoctoral fellowship at Georgia Institute of Technology (Atlanta, GA, USA), he became Assistant Professor (1994), and then Professor at the University Lyon 1. He was the leader of the group "Molecular Precursors and Inorganic Materials" in the Laboratory of Multimaterials and Interfaces (UMR UCBL / CNRS 5615). In 2003, he was appointed to the position of Lab Head up to 2010. In fall 2010, he joined the European Institute of Membranes of Montpellier (UMR CNRS 5635) with a part of his former group setting up the "Molecular Materials and Ceramics" group. In 2011, he has been appointed to his present position as Lab Head. Its main research interests lie in boron chemistry and in non-oxide advanced ceramics using the Polymer Derived Ceramics route, particularly new boron- and silicon-based materials. He was nominated junior member of the "Institut Universitaire de France" in 2003, and in 2011 has been appointed in "World Academy of Ceramics" as Professional Member (Academician) and is affiliated with the class "Science".

#### **Mikhael Bechelany**



Dr. Mikhael Bechelany obtained his PhD in Materials Chemistry from the University of Lyon (France) in 2006. His PhD work was devoted to the synthesis and characterization of silicon and boron based 1D nanostructures (nanotubes, nanowires and nanocables). Then, he worked as a post-doc at EMPA (Switzerland). His research included the fabrication of nanomaterials (nanoparticles and nanowires), their organization and their nanomanipulation for applications in different field such as photovoltaic, robotic, chemical and bio-sensing. In 2010, he became a Scientist at CNRS. His current research interest in the European Institute of Membranes of Montpellier (UMR CNRS 5635) in Montpellier (France) focuses on novel synthesis methods for metals and ceramics nanomaterials like Atomic Layer Deposition (ALD), electrodeposition, electrospinning and/or on the nanostructuring using natural lithography (nanospheres and/or membranes). His research efforts include the design of nanostructured membranes for health, environment and renewable energy.