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Asymmetric ceramic membranes from Langmuir–Blodgett deposition precursors: deposition of fatty acid salts on porous ceramic substrates

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Abstract

Nanoporous 7930 Vycor silica tubes and mesoporous and macroporous Anopore anodic alumina discs are examined as substrates for the multilayer Langmuir–Blodgett (LB) deposition of Cd, Mg, Zn and Ca salts of the arachidic and stearic fatty acids. Conditions for successful deposition are reported. Under appropriate conditions both mesoporous and macroporous Anopore aluminas allow for a full substrate coverage (maximum degree of deposition, $D_{d,\max} \rightarrow 1$), while a Vycor substrate imposes a $D_{d,\max} \leqslant 0.7$ and a mechanism explaining the observed $D_{d,\max}$ values is presented. The produced ceramic oxide–LB film composites are prototype precursors for gas-separating all-ceramic asymmetric membranes, following the application of an oxidative plasma treatment. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The formation of Langmuir–Blodgett (LB) monolayers and their transfer to compact substrates date back in the 1930s.[1] In more recent years, LB deposition has been of appreciable interest for applications in diverse fields such as microelectronics, biology and separations at the 0.5–10 nm scale.[2–5] The LB deposition of various new compounds on both compact and porous substrates has been reported.[3–5] LB deposition on porous substrates is usually attempted for polymeric substances, as the large molecular size of the latter allows for the easy bridging of the surface pores of the substrate. Nevertheless, at least one of the components of the LB substance/porous substrate pair is usually of purely organic character and, as a result, most composite membranes of LB origin are inappropriate for separations in harsh environments characterised by high temperatures and/or the presence of solvents and corrosive gases. On the other hand, all-ceramic membranes with superb performance under harsh conditions are highly sought-after materials for industrial separations.[6] Especially desirable for such applications, are *asymmetric* ceramic membranes consisting of an ultrathin ceramic separating layer, with pores belonging to the small nanopore or the micropore scale, and a ceramic porous substrate with pores at the nanoscale or larger. Commercially available ceramic substrate prototypes include nanoporous 7930 Vycor silica tubes (pore diameter: 40 Å), and mesoporous and macroporous Anopore anodic alumina discs, available at 200 Å, 0.1 and 0.2 μm mouth pore diameters.

Asymmetric membranes allow for the unique combination of the separation ability of the ultrathin top membrane layer and the large permeability of the larger pore substrate. However, asymmetric membranes are most often available in a *polymeric* form obtainable in a single basic processing step known as phase inversion.[7,8] In the case of an LB deposition, while processing is much more elaborate than phase inversion, the thickness of the separating top layer may be controlled with molecular precision, as each processing step leads to the deposition of a single layer of molecules.

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Here, we report on a rather general technique for the preparation of precursors of composite all-ceramic membranes through the Langmuir–Blodgett deposition of fatty acid salts on the aforementioned nanoporous, mesoporous and macroporous ceramic substrate prototypes. Such precursors are subsequently converted to a purely ceramic material through oxygen plasma oxidation, leaving an ultrathin layer of a ceramic oxide attached to the surface ceramic substrate. Structural characterisation[9] of Vycor substrate all-ceramic composite membranes will be reported in the second part of this study.[10,11]

The present report on the conditions for a successful deposition of fatty acid salts on porous ceramics is of obvious interest for the field of ceramic membranes but it also provides a positive answer to the question regarding the possibility of LB deposition of *small* amphiphiles on porous ceramic substrates. Notably, previous attempts to deposit fatty acid salts on different ceramic substrates[12] (macroporous discs with submicron sized pores and micron and submicron surface roughness) have not led to multilayer deposition, unless an intermediate polymeric or ceramic layer was used.

2. Experimental

2.1. Materials

Arachidic acid 99% pure, stearic acid >99% pure, $CdCl_2 > 99.99\%$ pure, $Na_2CO_3 > 99.5\%$ pure, $Zn(NO_3)_2.6H_2O$ 98% pure, $CaCl_2.xH_2O > 99.99\%$, $CH_3COONa.3H_2O > 99\%$ were obtained from Aldrich and $MgCl_2.6H_20$ 99% pure was obtained from Janssen Chimica. Chloroform >99% pure, stabilised with 0.75% C_2H_5OH was used as the fatty acid solvent.

Hydrophilic Vycor 7930 silica tubes (average porosity: 0.30, average pore diameter: 40 Å) were obtained from Corning. Prior to the depositions, the Vycor tubes were burned in the air at 550°C for 30 min for the full removal of any adsorbed organic compounds. A set of specially processed Vycor tubes was also prepared via heating in the air at 3°/min from room temperature to 780°C, followed by a 60 min isothermal step and a slow cooling under nitrogen. Flat Anopore alumina discs with a pore diameter of 200 Å, 0.1 and 0.2 μm were obtained from Whatman and used in the as received form.

2.2. LB apparatus, isotherms and deposition

A KSV-5000 single-trough, symmetric compression LB film-formation and deposition apparatus and a Milipore water subphase containing appropriate inorganic salts was employed for the depositions in the temperature range of 6–22°C. Preliminary work was performed with a LAUDA FW-2 LB apparatus. Deposition speeds in the range of 1–5 mm/min were examined. The apparatus (KSV model) consists of a Teflon trough, bearing a central well capable of accommodating samples of up to 10 cm long and two movable horizontal flat barriers with a hydrophilic polymer surface. The trough is filled to the bottom level of the hydrophilic barriers with the subphase fluid.

The subphase fluid is Millipore water also containing a soluble salt of a multivalent metal (e.g. $CdCl_2$, $MgCl_2$). The subphase water may also include a second salt (such as Na_2CO_3) for the purpose of pH adjustment. An amphiphilic fatty acid with a 15–20 carbon chain, is dissolved in chloroform (a fatty acid solvent non-miscible with the subphase) and few drops of the solution are spread carefully on to the surface of the subphase. Subsequently, the solvent is left to evaporate, leaving a 2-D gas-like dispersion of amphiphilic molecules on the surface of the subphase. By moving the barriers towards the center of the apparatus the initial gas-like 2-D dispersion of the amphiphilic molecules (Fig. 1, point G) is brought successively to the states of 2-D liquid (Fig. 1, point L) and 'solid' (Fig. 1, point S). Further compression leads to a collapse of the monolayer. This procedure leads to the determination of the isotherm shape. The shape of the isotherm depends on the amphiphilic substance and also on the nature and temperature of the subphase.

For the deposition process, the amphiphilic substance is spread again on the top surface of the chosen subphase and the barriers are moved until a surface pressure π_d comparable to that corresponding to point S (π_S) but smaller to it (typically $\pi_d \sim 0.8\pi_S$). When the surface of the substrate is of hydrophilic character, the substrate is immersed in the subphase prior to the spreading of the amphiphilic substance. The deposition

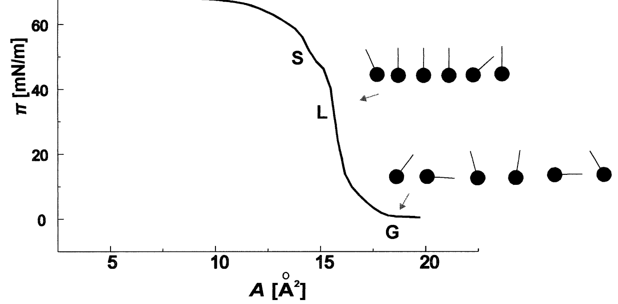


Fig. 1. LB isotherm for Cd arachidate ($CdCl_2$ subphase concentration: 1 mg/ml) at 20.5°C. π = surface pressure, A = area per molecule. G = 2-D gas phase, L = 2-D liquid phase, S = 2-D 'solid' phase (monolayer formation).

(LB film transfer) steps are carried under isobaric (constant π) conditions.

Deposition of the LB substance, such as the salt of a fatty acid, is achieved as the substrate moves at a constant rate perpendicularly to the fluid surface in and out of the subphase. A so-called Y-type deposition[3] is obtained when an LB layer is transferred *both* during dipping and retraction of the substrate and corresponds to a head to head and tail to tail molecular arrangement of the successive amphiphile molecular layers. If deposition is achieved only during the one type of steps (dipping or retraction), then the process is characterised as X or Z-type. Depending on the pH of the subphase a fatty substance may deposit either as an acid or as a salt of the fatty acid with the multivalent metal of the subphase. In general, the organisation of the LB deposited amphiphiles resembles, closely, that of the corresponding bulk crystalline phase and, as a result, a X or Z process may often lead to an LB structure of Y-deposition type of architecture, though the underlying mechanism is not well understood.[13]

The progress and quality of the deposition is monitored via a continuous recording of the degree of deposition, D_d. D_d is equal to LB film area transferred from the beginning of a deposition step *divided* by the total area of the substrate that will be made available for deposition during this step. Hence, when no deposition takes place at any point of a deposition step, D_d will remain equal to zero, while under conditions of ideal transfer, D_d will linearly rise during a deposition step from zero to one. $D_{d,\max}$ is the degree of deposition at the end of a deposition step.

Our reported D_d values are the recorded values corrected for the effect of barrier drift that is independent of transfer. The latter drift is recorded between deposition steps and its mean value is subtracted from the overall motion of the barriers during deposition. Successful LB transfers normally correspond to a corrected $D_{d,\max} = 1.00 \pm 0.05$. Somewhat larger $D_{d,\max}$ values (e.g. equal to 1.2) may be observed if upon transfer the LB substance reorganises to a more densely packed arrangement. Low $D_{d,\max}$ values (e.g. $D_{d,\max} \leqslant 0.5$) are usually indicative of poor transfer, large fluctuations and an overall tendency towards diminishing values. In the case of porous substrates we find that $D_{d,\max}$ values in the range of 0.5–1 are also possible. As will be discussed in more detail subsequently, when the $D_{d,\max}$ values in the 0.5–1.0 range remain *constant* or tend to *increase* with the number of deposited layers, the coverage of the substrate may be restricted to the solid part of the surface. Alternatively, a full or near full coverage of the substrate surface, including the porous part, is also possible, even though D_d is substantially smaller than 1, provided that upon deposition the amphiphilic molecules are capable of adopting a new, tilted arrangement.

3. Results and discussion

3.1. Deposition behaviour

Up to 2×19 deposition steps (each step corresponding either to a retraction or a dipping of the substrate) are applied to the porous ceramic substrates under examination. The deposition of a total of 10 layers is considered[4] as typically sufficient for flat substrate LB fatty acid transfer that will leave no film openings ('cracks') transversing the deposited material along its thickness. The deposition behaviour was examined for the arachidic and stearic fatty acids for both alkaline and weakly acidic subphase conditions. Examples of $D_{p,\max}$ values as a function of the deposition step are shown in Fig. 2.

Our most important deposition findings are described in Tables 1–3. Wherever a temperature *range* is indicated, it corresponds to a variety of deposition (subphase) temperatures tested within that range. X-Y refers to a deposition sequence proceeding successfully according to the X mode for a number of layers and subsequently shifting to a successful Y mode deposition, possibly as a result of the diminishing influence of the original substrate surface.

A general observation is that a nanopore Vycor substrate never leads to a $D_{p,\max}$ in excess of 0.7, while for both mesopore and macropore Anopore substrates $D_{p,\max}$ can reach 1. Nevertheless, even in the case of the Vycor substrate only those depositions that lead to a stabilised or near stabilised $D_{p,\max}$ value are listed. The significance of the $D_{p,\max} \leqslant 0.7$ level for Vycor will be discussed in detail in the following section. As Tables 1–3 reveal, ceramic membrane precursors can be easily prepared with Mg stearate and Cd arachidate amphiphiles and Ca and Zn arachidate amphiphiles are also good candidates. For practical applications we have to omit from the above group of amphiphiles Cd arachidate because of the health hazards associated with cadmium.

3.2. LB deposition on a Vycor substrate

The following observations need to be interpreted, regarding the behaviour of Vycor serving as a substrate for the transfer of LB film forming substances.

(a) Fatty acid salts deposited on Vycor with a $D_{d,\max}$ is circa 0.7, while for various anodic alumina substrates having much larger pores $D_{d,\max}$ is close to 1.0.
(b) With an increasing number of deposited layers the $D_{d,\max} \sim 0.7$ value for Vycor does not gradually diminish.
(c) LB layers of fatty acid salts, following plasma treatment lead to a significant narrowing of the majority of surface pores.[10,11]

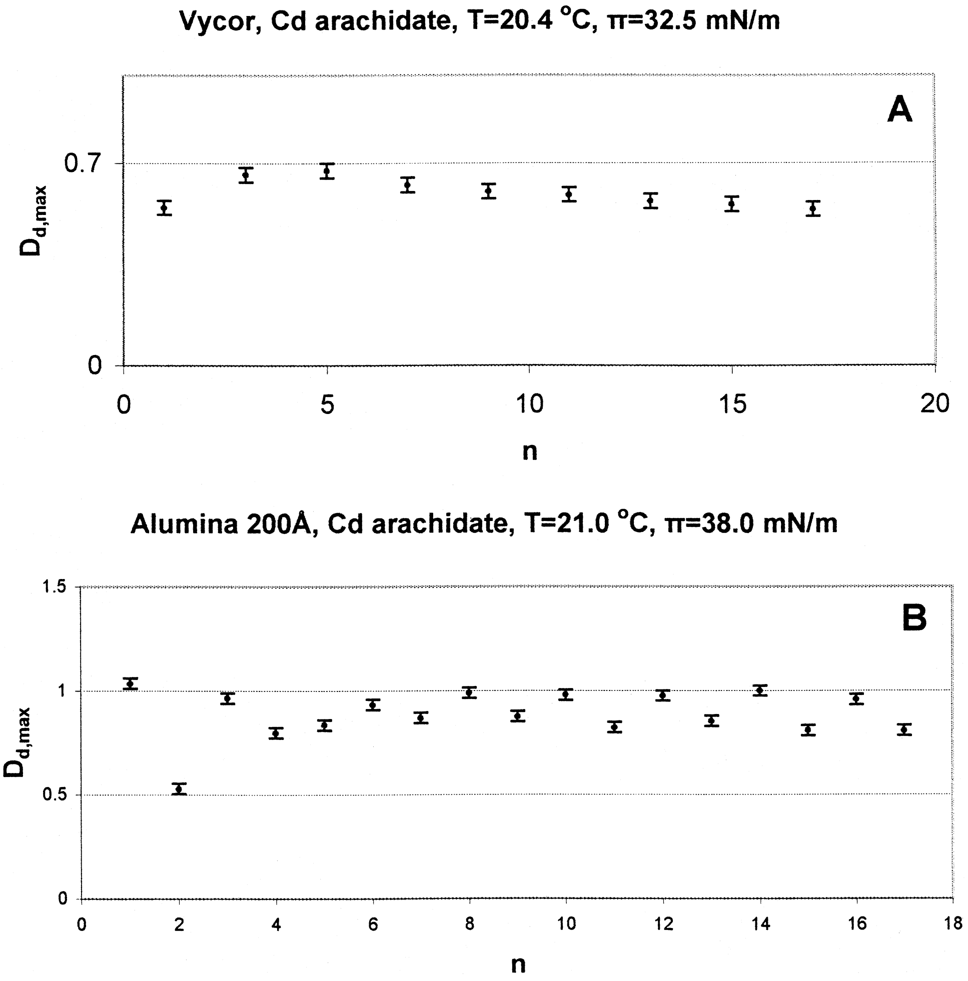


Fig. 2. $D_{p,\max}$ as a function of the number of deposition steps (n) for a Cd arachidate LB amphiphile and a Vycor (A) or a 200 Å Anopore (B) substrate. The deposition modes shown are X for the Vycor and Y for the Anopore substrate.

Table 1
LB deposition for a Vycor substrate

Metal ion	Acid	Subphase pH	T (°C)	π (mN/m)	$D_{d,\max}$	Deposition mode
Cd^{+2}	Arachidic	Mildly acidic	17–25	38, 32.5	0.5–0.7	Y
Cd^{+2}	Arachidic	Mildly acidic	17–25	38, 32.5	0.5–0.7	X
Cd^{+2}	Arachidic	Mildly acidic	17–25	38, 32.5	0.5–0.7	X–Y
Zn^{+2}	Arachidic	Mildly acidic	22–24	38, 32.5	0.3–0.5	X
Mg^{+2}	Arachidic	Alkaline	21–22	38	0.65	X
Ca^{+2}	Arachidic	Alkaline	15	32	0.55	X
Mg^{+2}	Stearic	Mildly acidic	22	32	0.35–0.55	X
Mg^{+2}	Stearic	Alkaline	19–23	38	0.65	X

Table 2
LB deposition for an alumina 2000 Å substrate

Metal ion	Acid	Subphase pH	T (°C)	π (mN/m)	$D_{d,\max}$	Deposition mode
Cd^{+2}	Arachidic	Mildly acidic	17–25	38	0.75–1	Y
Zn^{+2}	Arachidic	Mildly acidic	17–24	38, 32.5	0.85–1	Y
Mg^{+2}	Stearic	Alkaline	19–22	38	0.95–1	Y

Table 3
LB deposition for alumina 1000 Å and 2000 Å substrates

Metal ion	Acid	Subphase pH	T (°C)	π (mN/m)	$D_{d,\max}$	Deposition mode
Cd^{+2}	Arachidic	Mildly acidic	16–20	33	0.75–0.95	Y
Mg^{+2}	Stearic	Alkaline	17–19	38	0.7–1	X-Y

(d) $D_{d,\max} \sim 0.7$ for a Vycor substrate holds also for rigid-rod oligomers,[14] i.e. a class of compounds of structure and deposition habit completely different to that of the fatty acids (rigid molecules tend to deposit *flat* on a substrate). To be more precise $D_{d,\max}$ tends to be circa 0.70–0.75 for those oligomers while $D_{d,\max} \sim 0.6-0.7$ for fatty acid salts.

Observation (a) can be understood by noting that the porosity of Vycor $\varepsilon \sim 0.3$, and, consequently, $D_{d,\max} \sim 0.7 \sim 1-\varepsilon$. This implies that only the *solid* portion of the Vycor surface is used for the deposition. Hence, no metal ions are found immediately above the surface pores, while the opposite is true for the various anodic alumina substrates.

Observations (b) and (c) can be understood on the basis of a deposited structure model of Fig. 3A. The particular arrangement allows for a $D_{d,\max} \sim 1-\varepsilon$, though not necessarily exactly equal to $1-\varepsilon$. A structure such as that of Fig. 3 can be understood as a consequence of the fact that the metal ions 'decide' the packing on the surface pillars, while the organic chains adjust their tilt in order to find an optimal packing.[15] Accidentally, the diameter of a Vycor pore is comparable to twice the length of the fatty acid chains used, and this fact may also play a role in determining the tilt (or at least the *maximum* tilt of the fatty acid molecules). In addition, various $D_{d,\max} \sim 0.7$ arrangements differing with respect to the degree correlation of the tilt of adjacent LB stacks will lead to the narrowing of some of the pores only or of no pores at all (though they may

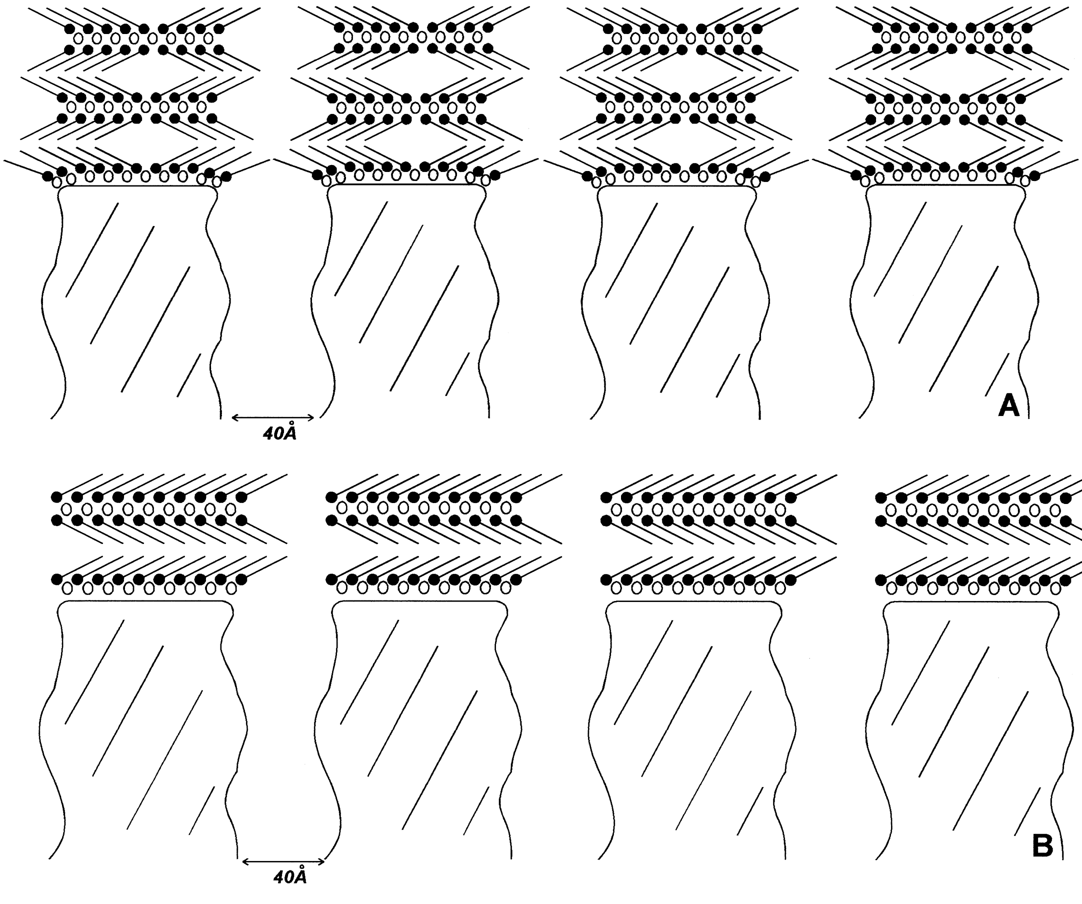


Fig. 3. Model for the arrangement of amphiphilic molecules on a Vycor surface, following LB deposition. (A) model corresponding to surface pore narrowing, (B) model corresponding to added surface tortuosity without surface pore narrowing.

introduce some surface tortuosity, Fig. 3(B)). Such arrangements are also compatible with observation (b), while a mixture of the various types of arrangements described above is also possible. In all cases of Fig. 3-type models, a short range relocation (occasional horizontal group-shifts of e.g. 10–20 Å) of the metal ions (metal oxide) can be postulated. Such a relocation will be part of the reorganisation following oxygen plasma treatment and can be used for the interpretation of observation (c). The towering of the Fig. 3 models makes the deposition sensitive to deviations from the normal to the substrate surface and provides a natural explanation for the frequent tendency of $D_{p,\max}$ to drop slowly with an increasing number of layers (Fig. 2(A)).

Observation (d) suggests that while models of the type shown in Fig. 3 may describe the basics of the *final* arrangement of the LB fatty acid layers on Vycor, there must exist a rather generic mechanism leading to a stable but limited (70%) degree of deposition when the substrate is Vycor. Such a mechanism could be specific to Vycor surface morphology and should be valid for a wide variety of molecules with the possible exception of very large molecules (*high* polymer molecules).

A mechanism of the desired type is shown schematically in Fig. 4. The case of fatty acid deposition is shown for convenience but it can be adapted to pertain to any relatively small molecules including rod-oligomers. This mechanism takes into account that the surface of Vycor includes large tree-like silicate protrusions that are capable of being raised or lowered, depending on the amount of water that is made available to them (see Fig. 5 and our recent work[16]).

According to the Fig. 4 model, while a Vycor LB substrate is still inside the water subphase, the silicate protrusions are attached to only one end of the Vycor surface and are found in an open configuration (as in Fig. 5(A)). Upon exposure of the surface to the air, the amount of water associated with the external surface of the Vycor is dramatically reduced. As a result, the tree-like silicate protrusions of the deposition surface of Vycor undergo an orientational transformation and become attached to the surface (as in Fig. 5(b)). This orientational transformation of the silicate entities also forces the portion of LB film already deposited on them to move closer to the Vycor surface. It is also possible that this process introduces a tilt to the attached molecules of

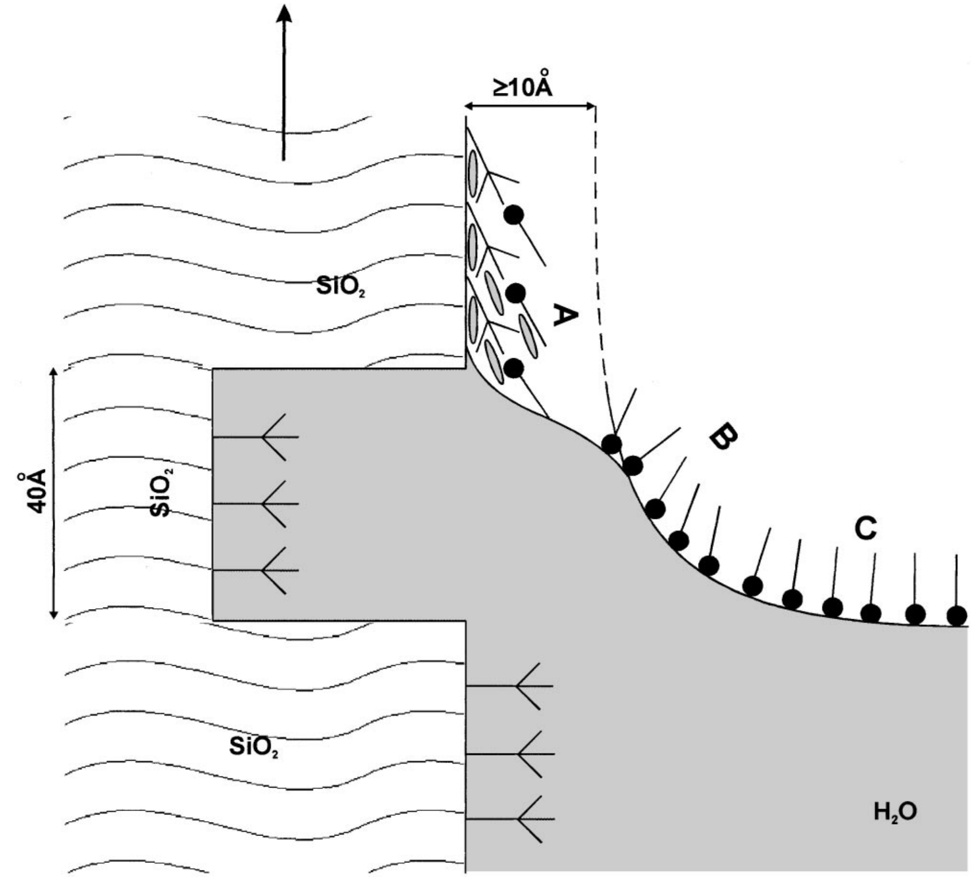


Fig. 4. Model of the LB deposition process for small molecules and a Vycor surface. Group A: Amphiphilic molecules lying above the solid portion of Vycor. Group B: Amphiphilic molecules lying in the vicinity of a Vycor pore. Group C: Amphiphilic molecules in their standard, prior-to-deposition configuration (horizontal LB–water interface). The arrow at the top indicates the direction of motion of the Vycor substrate.

the LB film. It may be postulated that that attached on the silicate entities portion of the LB film will be found at least 10 Å closer to the Vycor surface, than expected on the basis of a smooth extension of the non-attached portion of the LB film (Fig. 4). Those two distinct levels of LB material (group A and group C) will cease to be connected smoothly when a surface pore is exposed to the LB film (group B). At this point, the LB film exists at two distinct levels and possibly two orientations; Group B is forced to choose a side, and retracts to remain in contact with its natural extension i.e. group C. The pore will remain non-LB covered, though no amphiphiles will fall into the pore gap, at least on a massive scale. LB coverage of the Vycor surface will continue when a solid portion of the surface is exposed again to the LB film lying on the subphase. As a result, a $D_{p,\max} \sim 1 - \varepsilon$ will be achieved.

The same model can also explain why subsequent LB layers follow the $D_{p,\max} \sim 1 - \varepsilon$ pattern as well. During a subsequent deposition, while the substrate is inside the water, the surface silicate protrusions become again hydrated and rise to define the surface dimensions of the substrate. Upon leaving the subphase, the surface of the Vycor substrate transforms again, i.e. the silicate protrusions become attached to the solid and the LB pattern of transfer for the first layer is repeated.

An additional experiment pertinent to our model of Fig. 4, is the LB deposition on a modified Vycor surface. We have opted to heat Vycor at 780°C, i.e. near the maximum temperature that the porosity remains intact (ε starts dropping at temperatures $\geqslant$800°C). Between 600 and 800°C Vycor undergoes a drastic loss of OH[17] and it may be inferred that at 780°C the hydroxylated fine silicate surface protrusions would be greatly reduced or eliminated. While our Cd arachidate LB deposition findings are inconclusive, parallel work with the siloxanic oligomers (which lie flat and can bridge a pore more easily) has led to a clear raise of

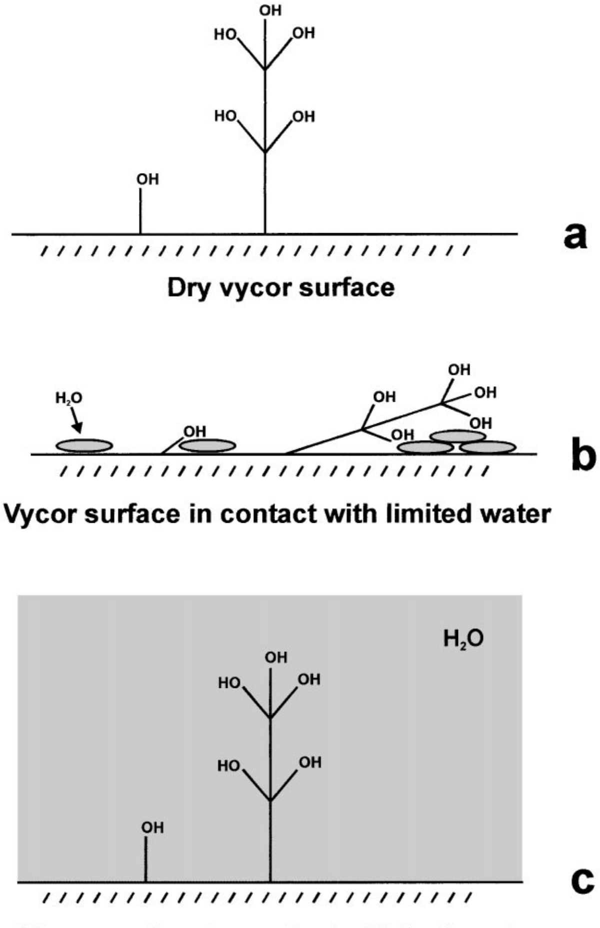
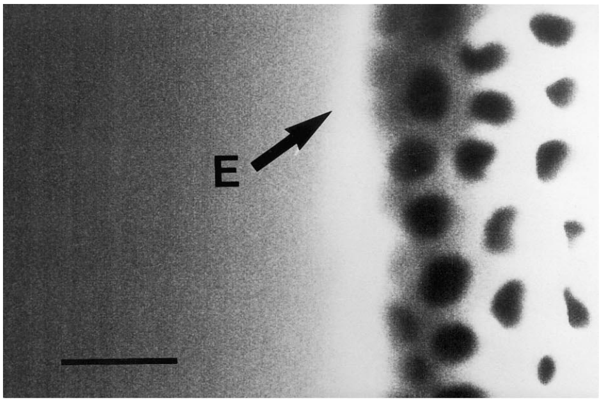
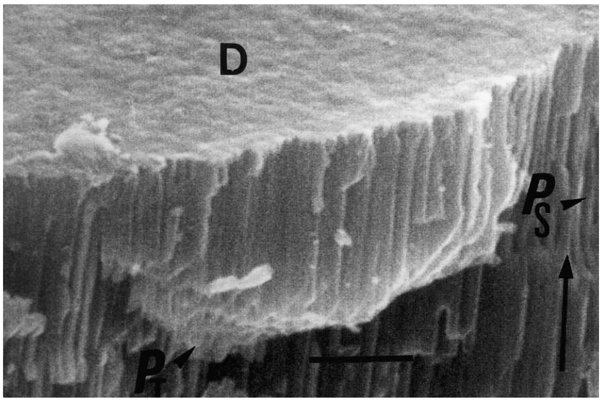


Fig. 5. Interaction of water with a Vycor surface bearing silicate protrusions.



(a)



(b)

Fig. 6. Complete surface modification of ceramic substrate after LB deposition and plasma treatment. A fully inorganic asymmetric membrane was produced from an Anopore alumina substrate with $d =$ 2000 Å and plasma-oxidised 17 LB-layer deposition of Cd arachidate. A: Membrane top view: Left (compact) side bears the deposition. Right side bears no deposition. E is the edge of the deposition. Scale bar = 0.6 μm. B: View of the membrane section. D is the continuous deposition on the top of the alumina. Long arrow is parallel to the straight pores of the alumina substrate. P_S is a side view of cleaved substrate pores. P_T is the substrate porous structure as revealed by an accidental cleavage of the substrate in a direction that is not parallel to the pore axis. Scale bar = 2 μm.

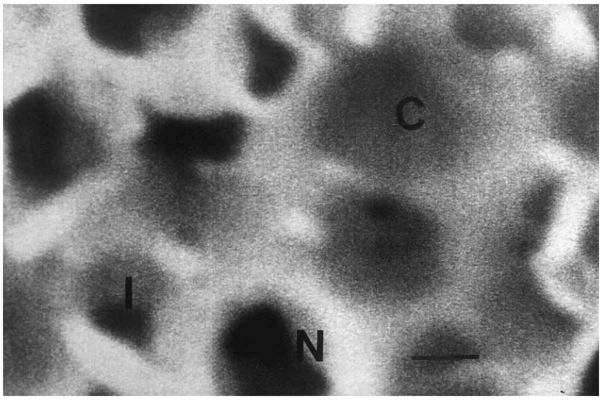


Fig. 7. Thin partial deposition of Cd arachidate on an anodic alumina with $d = 2000$ Å. Some of the pores are completely covered (C), while others are partially covered (P) or non-covered (N). Scale bar = 0.2 μm.

$D_{d,\max}$ from 0.75 to 0.85,[14] a change that is compatible with the hypothesis that the observed $D_{d,\max}$ values ca. 0.7 reflect some special behaviour of the silicate surface protrusions of the standard Vycor surface.

3.3. *Asymmetric ceramic membranes from plasma treated LB / ceramic precursors.*

A fully satisfactory, i.e. completely covered, all-ceramic composite membrane sample appears in Fig. 6. For comparison, a non-satisfactory sample characterised by incomplete coverage appears in Fig. 7. In both cases, the substrate used is the one with the largest pores (Anopore alumina with a $d = 2000$ Å) examined and, hence, the most difficult to cover porous substrate, at least in principle. The photographs reveal that a full coverage is preserved, even after the oxygen plasma is applied. Details of the plasma processing applied to various samples and the pore structure characteristics of Vycor substrate samples, as determined by a wide range of permeability methods of membrane characterisation[9] will be given in the second part of this work.[10]

Our findings combined with earlier observations[12] suggest that porous ceramic surface properties (roughness and interaction of the substrate with the subphase) rather than pore size (at least for $d_{\text{pore}} \leqslant 0.2$ μm) control the quality of LB transfer, at least for small and moderately sized molecules. Anodic alumina that may be thought as having a smooth surface leads to $D_{d,\max} = 1$. Vycor is an intermediate example for which the surface 'breathing' mechanism limits $D_{d,\max}$ to $1 - \varepsilon$, while porous ceramic substrates with a rough surface lead to $D_{d,\max} \sim 0$.

4. Conclusions

Precursors of all-ceramic asymmetric membranes appropriate for gas separation may be prepared through multilayer LB deposition of fatty acid salts on nanoporous Vycor silica and Anopore alumina substrates.

The Vycor surface imposes a degree of deposition circa 0.7 which is the result of the disruptive action of silicate surface protrusions on the LB film, at the moment of deposition.

For small and moderately-sized LB molecules and a substrate pore size $\leqslant 0.2$ μm, the quality of deposition depends primarily on the surface properties of the solid portion of the porous ceramic substrate.

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