

Methods for a fast evaluation of the nano-porosity of thin coatings for the development of plasma polymeric membranes

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Abstract: The key to developing high performance plasma polymeric membranes using plasma enhanced chemical vapour deposition (PECVD) is to control the nano-porosity (pore sizes < 2 nm) of the coatings. This paper contrasts cyclic voltammetry (CV) and physical etching with atomic oxygen as methods to measure the porosity of thin coatings focusing on their suitability as a fast coating evaluation tool for coating development. Both methods proved to be viable options for quantitatively measuring porosity.

Keywords: PECVD, coating porosity, membranes, cyclic voltammetry, etching

1. Introduction

The fabrication of plasma polymers by PECVD as membranes for gas separation has not received much academic research attention in the last decades, possibly due to the low separation performance of so far produced coatings in comparison to established asymmetric composite membranes with polymeric films [1–4]. However, this is due to change, with recent advances in the investigation of functional PECVD coatings regarding coating porosity [5–12]. Adjustability of the coatings' nano-porosity (pore sizes < 2 nm) and the absence of micro-pores are necessary for producing membranes with defined gas separation properties. One obstacle for the development of plasma polymeric membranes is that the measurement of the coatings porosity is time consuming. Methods like spectroscopic ellipsometry or especially positron annihilation spectroscopy (PAS) lack broad availability; gas permeation measurements of a single specimen can take several hours upon completion. Hence, a fast exploration of the large parameter space given for plasma processes is not possible. The coatings investigated in this paper were therefore analysed with two methods for a quick evaluation of the coatings porosity to demonstrate their feasibility for the coating development process, especially in its early stages.

Cyclic voltammetry (CV) is an analytical method to determine electrochemical processes within a three-electrode-arrangement. The amount of interfacial electron transfer depends on the exposed contact area of the working electrode to a redox active electrolyte solution. A coating on the working electrode reduces the exposed contact area to the accumulated area of pores in the coating. Hence, the measured current can be correlated with pores in the coatings [5,6].

Da Silva Sobrinho et al. proposed a method to visualize coating defects by etching a polymeric substrate (e.g. Polyethylenterephthalat, PET) on which the coating is

applied [13,14]. The etching process is performed by oxygen plasma treatment. PET is sensible towards etching by oxygen, whereas a PECVD coating produced by a silicon-containing monomer gas is almost not affected by it. Thus, the inorganic layer of the coated samples functions as a mask and reactive oxygen can only reach the PET surface via pores and defects, thereby locally etching the unprotected polymer surface, creating crater like structures. These craters can then be investigated using field emission electron microscopy (FESEM) [8]. All specimens are coated with a thin (thickness of ca. 3 nm) gold layer to achieve a conductive surface.

2. Experimental

Figure 1 shows a schematic representation of the plasma process reactor for the coating application using pulsed microwave plasmas. Four quartz glass tubes (duo plasma lines), which are located at a distance of 165 mm from the substrate holder introduce pulsed microwaves with a frequency of 2.45 GHz into the reactor. Four magnetrons with a maximum peak power of 4000 W are used for power supply.

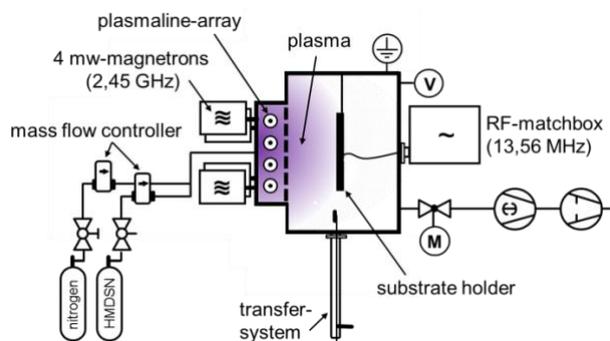


Fig.1 plasma process reactor for pulsed mw-plasma excitation

Details on the low-pressure chamber for PECVD are described elsewhere [9].

Two plasma polymers were produced for comparison, using the monomer Hexamethyldisilazan (HMDSN) (table 1). As the varied parameter the microwave power (MW) input into the plasma was chosen, as it is well known, that it substantially affects the coatings growth mechanisms and thus, its porosity [7,9].

Table 1 plasma process parameters

coating	HMDSN/N ₂	MW [W]	pulse on/off [ms]	time [s]	process pressure [Pa]	coating thickness [nm]
MW1	0.8	1000	3/40	63	15	20 ± 2
MW2	0.8	2000	3/40	8	15	20 ± 2

The thickness of both investigated coatings was adjusted by deposition time to be 20 nm for better comparability. The according deposition rates were deduced from measuring coatings with a thickness in the range of 100 nm for all given compositions on Si-Wafers by means of stylus profilometry (Dektak 6m Stylus Profiler, Veeco Instruments Inc., USA). Constant deposition rates for all coatings are assumed. Three samples for each coating were prepared and analysed.

For CV measurements a three-electrode electrochemical cell is chosen, consisting of a working electrode (ca. 200 nm ultra-smooth gold coating on polished Si-Wafers) with an exposed area of 19.6 mm², a saturated calomel reference, a platinum counter electrode and a custom-made cell. An aqueous electrolyte solution of 10 mM ferrocyanide (K₄[Fe(CN)₆]) was used, as it represents a simple redox couple and no complications due to post chemical reactions can be expected. The potential range was set between -0.2 V and 0.9 V with a scan rate of 100 mV s⁻¹. Two samples were measured for each coating to check for reproducibility.

3. Atomic Force Microscopy (AFM)

AFM images of both coatings on polished Si-Wafers were obtained to evaluate the growth mechanisms before porosity measurements (Figure 2).

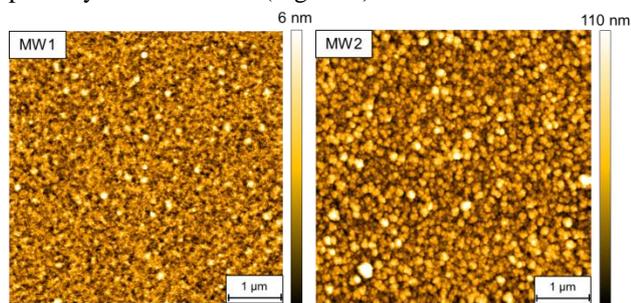


Fig.2 AFM images of both investigated coatings

Coating MW2 exhibits a far greater surface roughness with $R_a = 14.3 \pm 0.7$ and a more coarse-grained microstructure than coating MW1, which surface appears comparably smoother with a $R_a = 0.6 \pm 0.1$. According to Grundmeier et al. [7] and Durst et al. [15], bigger grain

sizes can lead to the formation of pores at grain boundaries, indicating a higher porosity of coating MW2.

4. Cyclic voltammetry

Figure 3 shows the CV results for an uncoated gold reference and for both investigated coatings. The reference measurement shows the typical graph for this redox couple. Measured currents for both coatings decrease significantly, proving that the active surface where the redox reaction can occur is reduced by the coatings. Comparing to MW1, coating MW2 furthermore exhibits far greater measured currents, suggesting a larger accumulated area of pores present in this film.

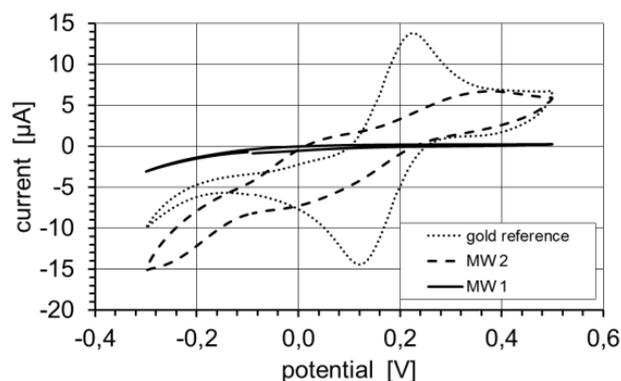


Fig.3 CV results of coatings MW1 and MW2

The relative surface coverage of the coating on the working electrode was calculated by integrating the area under the obtained graphs and correlating the values to the reference [16]. For MW1 the total coverage of the working electrode by the coating is calculated to be about 97 %, while for MW2 only a value of ca. 74 % is achieved. It is possible that nanoparticles are already formed in the plasma bulk under higher excitation power, before being adsorbed on the substrate surfaces. This could lead to the more coarse-grained surface structure as of MW2. It could also lead to possible nanoscopic pathways at the grain boundaries, implying a higher porosity of this coating.

5. Physical etching with atomic oxygen

Both coatings were applied on PET substrates for these investigations. Figure 4 presents high resolution FESEM images of both coatings. MW2 shows a more granular surface than MW1 exhibits, confirming the AFM image results. Furthermore, possible pores in coating MW2 can be observed as dark dots at the grain boundaries in the image.

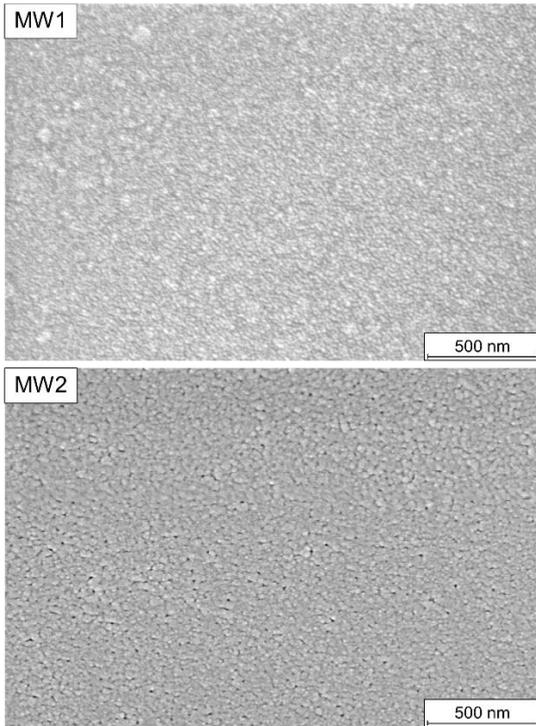


Fig.4 FESEM images of both investigated coatings

Both coatings were then subjected to a microwave-excited oxygen plasma with an RF-Bias for one hour. As can be seen in Fig. 5, crater-like structures formed on both specimen's surface after etching. As expected, coating MW2 presents a far greater number of craters than MW1. Each crater represents an initially present pore, whose size was greatly increased due to the etching process and removal of the underlying polymeric material. With an image recognition software based on the MATLAB Image Processing Toolbox, the number of defects can be easily quantified using binary images. 10 SEM images with an investigated surface of $61 \mu\text{m}^2$ were acquired of each coating for defect analysis and two samples for each set of parameters were investigated. MW2 exhibited a pore density of $0.111 \pm 0.031 \mu\text{m}^{-1}$, while MW1 only showed a density of $0.032 \pm 0.008 \mu\text{m}^{-1}$ on the given image surfaces. Furthermore, a difference in pore sizes can be observed, as shown by high resolution images of single pores in Fig. 5. After the same etching process exhibits coating MW1 pores with an average diameter of roughly 200 nm. The pores seen in coating MW2 have diameters in the range of about 1 μm , hinting at initially bigger pore sizes for this coating. The images also reveal a dark circle around the pores, possibly due to an undermining of the coating in the etching process.

The original size of the pores can generally be estimated by capturing series of images of specimens subjected to different etching times, observing the growth rate of the pores. Assuming a linear growth, the initial pore size can then be deduced by linear interpolation to $t_{\text{etching}} = 0 \text{ s}$ [11]. With known initial pore sizes, an estimation of the

accumulated pore surface can be given. These measurement series are fairly time-consuming and were therefore not performed in this work, as the current focus lies on the fast evaluation of coating porosity.

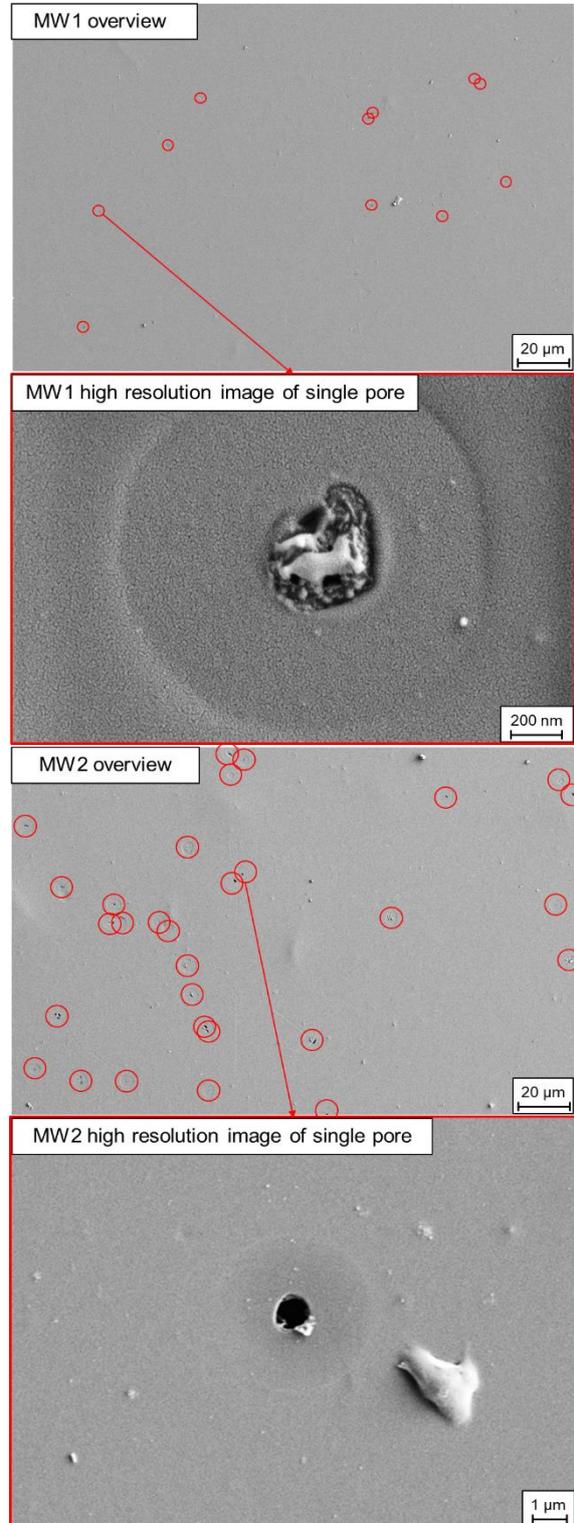


Fig.5 physical etching of both investigated coatings

6. Conclusion

The presented results prove that the porosity of thin plasma polymerised coatings can be controlled by specific adjustment of process parameters. Both evaluated methods can be viable options for investigating the porosity in the coatings.

A major advantage of cyclic voltammetry is that the measurements can be completed and repeated within minutes, delivering fast quantitative results. One limitation of this method is that no information on the pore sizes can be obtained, but only on their accumulated surface area.

The method of physical etching with atomic oxygen combined with electron microscopy shows good practical potential in evaluating coating porosity, with regard to quantifying the pore density and a first evaluation of the pore sizes. It also has the potential to estimate initial pore sizes, though this remains to be a rather cumbersome and time-consuming process, especially since the same position on the specimens has to be found under the electron microscope in every turn.

It should be noted, that the accumulated pore area of coating MW2 is far greater in the CV measurements, than what could be estimated from the FESEM images of the etched specimens. It could be possible, that a great number of nano-scale pores is present in the MW2 coating, which couldn't be enlarged sufficiently to be visible in the microscopic images, even after 1 hour of etching process.

Future work should include a correlation of porosity values from the two evaluated methods and gas separation property measurements, as well as spectroscopic ellipsometry or positron annihilation spectroscopy (PAS).

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