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Diffusion rate of hydrogen peroxide through water-swelled polyurethane membranes

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A B S T R A C T

In our efforts to design an optical sensor for hydrogen peroxide, we have realized the importance of knowing/controlling the diffusion of hydrogen peroxide to the indicator, especially in the case of an irreversible indicator. Since we found little literature data, we decided to test the permeability of hydrogen peroxide in commercially available polymers, focusing on the polyurethanes HydroMed™ and HydroThane™, which are commonly used for immobilization matrices in optical sensors. Measured values are between $5.12 \ 10^{-9} \pm 8.50 \ 10^{-10}$ and $2.25 \ 10^{-6} \pm 1.00 \ 10^{-7} \ cm^2 \ s^{-1}$.

1. Introduction

Hydrogen peroxide (H_2O_2) is a reactive oxygen species (ROS) of major importance in living organisms [1], where it has two important roles. On the one hand, H_2O_2 is involved in vital processes, such as cell signaling [2] and defending against invading microbes [3,4]. On the other hand, it is associated with cell death and aging [5,6], and mismanagement of ROS results in oxidative stress [7]. Thus, it is of interest to monitor H_2O_2 concentrations in biological systems, and various options exist for measurements in- and outside of cells [8,9]. One important challenge for most of the published probes for H_2O_2 is the lack of reversibility [8,10–12], which ends up reducing the life-time. A possible solution might me to apply a polymeric membrane that limits diffusion of H_2O_2 to the probe. To our knowledge there is little literature on permeability of H_2O_2 in polymers, examples are given in Table 1, and seems to have been mostly investigated for use in electrochemical enzymatic glucose sensors [13–15]. However, there is often focus on selectivity compared to 'interfering species' [14,16,17], and diffusivities are reported in two different units, either as a diffusion coefficient ($cm^2 \ s^{-1}$) [13,15] or as a percentage of the response of membrane covered electrode to a bare electrode [17,18].

Diffusion of small molecules in polymers is dependent on the glass transition of the polymer, and the diffusion mechanism for two cases (below or above) differs. When the diffusion rate of the small molecule is much smaller than the relaxation rate of the polymer, the diffusion process is Fickian [19]. Fick's first law describes diffusive mass flux as a function of diffusion coefficient and difference in solute concentration. Consequently, the driving force is the gradient in concentration (chemical potential) [20]. In the case of hydrogels, the solute transport is mainly with-in the aqueous regions in the gel, and is generally dependent on the cross-linking density, solute size, and fraction of water in the gel [21–23]. As mentioned above there is only sparse knowledge of the diffusion rate of H_2O_2 in polymer membranes, and we have embarked on an effort to characterize the transport of H_2O_2 in selected polymeric membranes.

Polyurethanes are widely applicable polymers and very versatile because of a three component system for the polymer that allows great variety in building blocks. The components are a polymeric diol, diisocyanate, and a chain extender (low molecular diol), which forms incompatible soft- and hard segments [24–26]. The hard segments have high T_g or T_m, and the soft segment have a relatively low T_g [27]. Due to the incompatibility, the two segments separates on a microphase level, and the degree of this segmentation affects the material properties of the polyurethane [24,28]. Correlated to this is the type of soft segment (polyester or polyether) and chain length [29,30], and the symmetry of diisocyanate and type of chain extender [31,32]. We have chosen to focus on two lines of commercially available polyurethanes for this study, HydroMed™ ([1]) and HydroThane™ ([2]).

Nafion® is commonly used as polymer electrolyte membranes in fuel cells. It is a random copolymer with a tetrafluoroethylene backbone and a perfluoroalkyl ether side chains terminated with sulfonic acid groups [33]. Water is transported through the membrane in hydrophilic

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Table 1
Literature data for H_2O_2 permeability in polymers.

Polymer	D_e [$cm^2 s^{-1}$]	Source
Polypyrrole	5,00E-09	Gros 1995 [13]
Poly-*o*-phenylene-diamine.	5,00E-09	De Corcuera 2005 [40]
Humic acids/ferric cations (HAs/Fe^{3+}) membranes	4,80E-09	Vaddiraju 2009 [15]
Poly (diallyldimethyl-ammonium chloride) (PDDA) and poly(styrene sulfonate) (PSS/PDDA)	1,00E-10	Vaddiraju 2009 [15]
Polymethyl methacrylate (PMMA)	5,83E-06	Herman 1963 [38]
Polypropylene	5,50E-09	Radl2011 [41]
	D_e [g. H_2O_2/ 0.001 in./ 100 in.^{2}/24 h]	
Polyvinyl chloride	2.5–8	Dietrick 1959
Polyester	3.3	[42]
Low-density polyethylene	0.10	
Polyvinylidene chloride	0.03	

domains [34,35], and though it varies, the water diffusivities in Nafion® reported in literature seem to be fairly high. Also, the presence of water in a polymer electrolyte membrane is important for achieving high proton conduction [36]. [Zhao et al. [34]] reports a table on literature data. Additionally, Nafion® have been applied as a membrane in combination with cellulose acetate for selective diffusion of H_2O_2 over negatively charged species [14]. Therefore, we speculate that Nafion® might be used to exclude negatively charges ROS, and decided to test the H_2O_2 permeability of a Nafion® 117 membrane ([3]).

With the end goal of designing optical sensors we decided to investigate the permeability of H_2O_2 in various commercially polymers, for which data is here reported.

2. Experimental approach

2.1. List of chemicals

All chemicals were used as received. See SI for additional information. HydroMed™ and HyroThane™ polymers were kindly provided by Technical University of Graz, Institute of Analytical Chemistry and Food Chemistry. A piece of Nafion® 117 membrane was kindly provided by DTU, Department of Chemistry. PMMA was kindly provided by University of Copenhagen, Department of Biology, Marine Biological Section.

2.2. Polymer film preparation

Films from HydroMed™ were prepared by knife coating a 10% solution in THF onto a glass slide using a 10 mils bar. To produce film of different thicknesses, the knife coating was repeated after the THF had evaporated. When the film had dried, the film was cut to fit the diffusion cell (described below), and removed from the glass slide by swelling in deionized water. HydroThane™- and PMMA films were prepared in a similar way from 5% solutions in THF and 10% solution in DCM, respectively.

A piece of Nafion® 117 membrane was cut in approximately $0.5 \times 0.5\ cm^2$ samples, boiled in 3% H_2O_2 solution, boiled in deionized water, then 0.5 M sulfuric acid, and deionized water. Each of the boiling steps took at least an hour. The hydrolyzed Nafion® was kept in deionized water until tested for H_2O_2 permeability.

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[3] http://www.nafionstore.com/store/products/60/Nafion-Membrane-N117

2.3. Polymer film thickness

For PMMA and Nafion® 117 the thickness of the membranes is determined with a micrometer screw gauge (precision of 0.001 mm) of films swelled in water. For HydroMed™ and HyroThane™ polymers the formed films were too soft to measure with the micrometer screw gauge. Therefore, the thickness is measured on dry samples with a confocal laser scanning microscope (LSM 700, Zeiss) by measuring the difference in the confocal z-axis at the edge of the polymer film. Using the microscope software package (Zeiss Zen 2012 Black edition), a series of z-stacks of reflected light with a height of 0.38 µm were acquired, and the intensities were used to obtain the thickness in the software "ImageJ". Then, the degree of swelling was determined for the polymer gravimetrically using the equation: "deg. of swell. = m_{wet}/ m_{dry} "where m_{dry} is the mass of the dry polymer and m_{wet} is the mass of the swelled polymer. Finally, the thickness of the swelled films is obtained by assuming isotropic swelling.

2.4. Diffusion tests

The Diffusion cells contain two compartment separated by a polymer film. The tested film were placed in the cell, and checked for leakage by filling one of the compartments with deionized water for 30 min. If no liquid leakage was observed, the second chamber was similarly filled with deionized water for another 30 min. At the start of the experiment, the acceptor cell was filled with 200 ppm acetanilide in H_2O, and the donor cell was filled with a solution of 1 M H_2O_2 and 200 ppm acetanilide in H_2O [37]. Both compartment contained 8 mL and were stirred with Teflon™ magnets during the experiment. Concentrations of H_2O_2 were determined by titrating 25 µL H_2O_2-solution (from the cells) in 0.05 M sulfuric acid with 0.006 M Potassium permanganate solution using a micro-pipette (precision of 0.001 mL). At each sampling time, the concentrations in the donor- and acceptor chamber were determined by three titrations and reported as the average with standard deviations. The concentration evolution is then fitted to the mass balance:

$$ln \frac{c_0}{c_D(t) - c_A(t)} = \beta \frac{D_e}{l} t, \ \beta = A_0 \left(\frac{1}{V_D} + \frac{1}{V_A} \right)$$

where c_0 is the initial H_2O_2 concentration in the donor compartment; $c_D(t)$ and $c_A(t)$ are concentrations at time (s) in the donor- and acceptor chamber, respectively; $c_A(0) = 0$; V_D and V_A are solution volumes (mL); A_0 is the area (cm^2) of the polymer film exposed to the solutions; l is the film thickness (cm); D_e ($cm^2 s^{-1}$) is the effective diffusion coefficient of H_2O_2 in the polymer.

3. Results and discussion

The main goal of this work was to measure H_2O_2-permeability in various commercially available polymers, which are commonly used as immobilization matrices of indicator dyes. The results are reported in Table 2. As an example of a typical concentration evolution, Fig. 1 shows the data for HydroMed™ D4, and data for all permeability values in Table 2 are reported in Supporting Information (Figs. 1–17). We estimate that permeability in the range of 10^{-7} to $10^{-11}\ cm^2 s^{-1}$ is needed to extend sensor life-time, and compared to this, the measured values are either in the high end of the range or too high.

To assess the uncertainty of the obtained data, permeability of three polymers were measured twice. Hydromed™ D6 (entry 4 and 5), HydroThane™ H5 (entry 7 and 10), and HydroThane™ H25 (entry 9 and 15) in Table 2. The biggest relative difference is seen for H5, however, the R^2 values are fairly low for both measurements, and therefore the exact value for D_e is a little questionable. For the D6 and H25, the effective diffusion constants are approximately in agreement, but still outside the deviations of the fits (the ± error reported in Table 2).

Table 2

Measured effective diffusion coefficients. Polymers named D1-D7 are HydroMed™, and polymers named H5-H25 are HydroThane™.

Polymer	Deg of swell	De [cm² s⁻¹]	± Error [cm² s⁻¹]	R²
D1	3.971	1.56E-06	7.00E-08	0.9861
D3	2.761	9.27E-07	5.30E-08	0.9788
D4	2.707	7.44E-07	1.70E-08	0.9962
D6	7.652	2.25E-06	1.00E-07	0.9886
D6	7.652	1.63E-06	3.00E-08	0.9981
D7	1.454	8.31E-07	2.50E-08	0.9931
H5	1.047	9.93E-09	1.09E-09	0.6906
H15	1.121	9.37E-09	2.80E-09	0.9902
H25	1.230	7.72E-07	3.00E-08	0.9947
H5	1.047	5.12E-09	8.50E-10	0.6984
H5 and H25 (4:1 wt/wt)	1.084	1.36E-08	9.80E-10	0.8977
H5 and H25 (3:2 wt/wt)	1.120	4.02E-08	1.80E-09	0.9660
H5 and H25 (2:3 wt/wt)	1.157	1.48E-07	6.00E-09	0.9673
H5 and H25 (1:4 wt/wt)	1.194	2.03E-07	9.70E-09	0.9058
H25	1.230	6.28E-07	4.00E-08	0.9719
Nafion® 117		1.50E-06	7.00E-08	0.9606
PMMA		5.76E-07	4.60E-08	0.9595
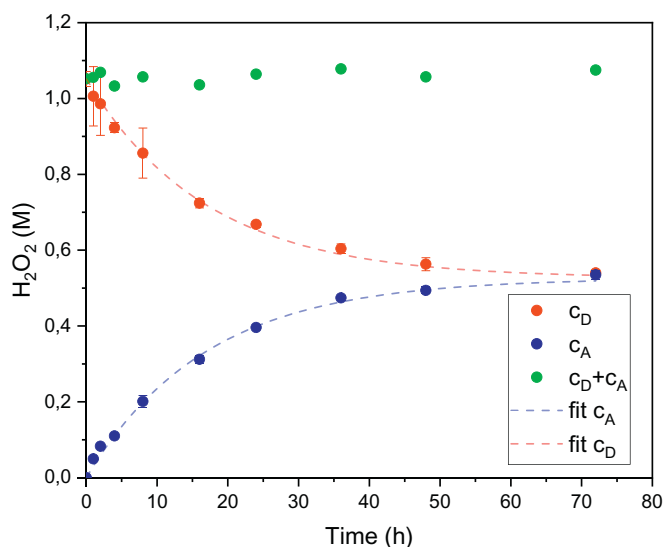
Fig. 1. HydroMed™ D4; $l = 1.423778 \cdot 10^{-3}$ cm; $c_0 = 1.052$ M; $A_0 = 0.1256$ cm²; $\beta_{max} = 0.0314$ cm⁻¹; $D_e = 7.44 \cdot 10^{-7} \pm 0.17 \cdot 10^{-7}$ cm² s⁻¹; $R^2 = 0.9962$.

The ± errors are obtained from the fit, and describe deviation of the data from the fit. However, in the fit, the values for initial concentration (c_0) and film thickness are fixed. c_0 is measured with the same precision as the other data points, and have a similar standard deviation. For the film thickness, the effects of errors are more impactful, as seen from the direct correlation with D_e. The thickness of the film is determined using two assumptions, isotropic swelling and uniform thickness across the membrane. For instance, if the film is slightly thicker in middle compared the edges, the error is multiplied by the degree of swelling (largest for D6), which then affects D_e directly without being expressed in the results.

Due to the high water permeability of Nafion® [34], we theorized that it too is highly permeable to H_2O_2. This hypothesis is confirmed by the obtained diffusion coefficient ($D_e = 1.50 \cdot 10^{-6}$ cm² s⁻¹). Similarly, PMMA was tested to compare to a value found in the literature, and we have measured an effective diffusion coefficient one order of magnitude lower. Herman and Giguére [38] report a value of 5.83
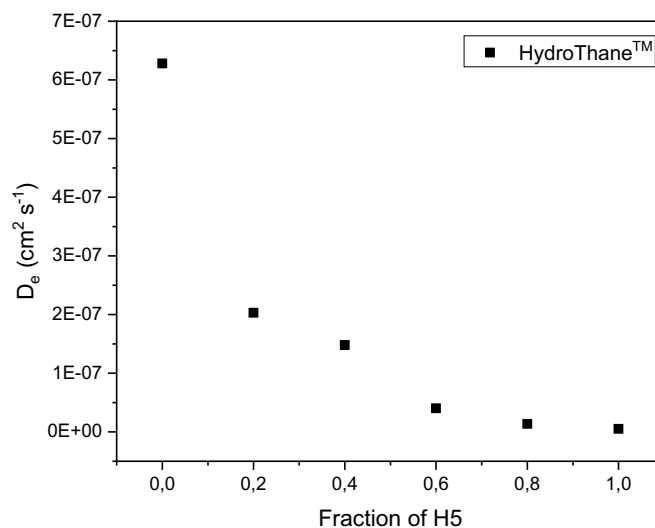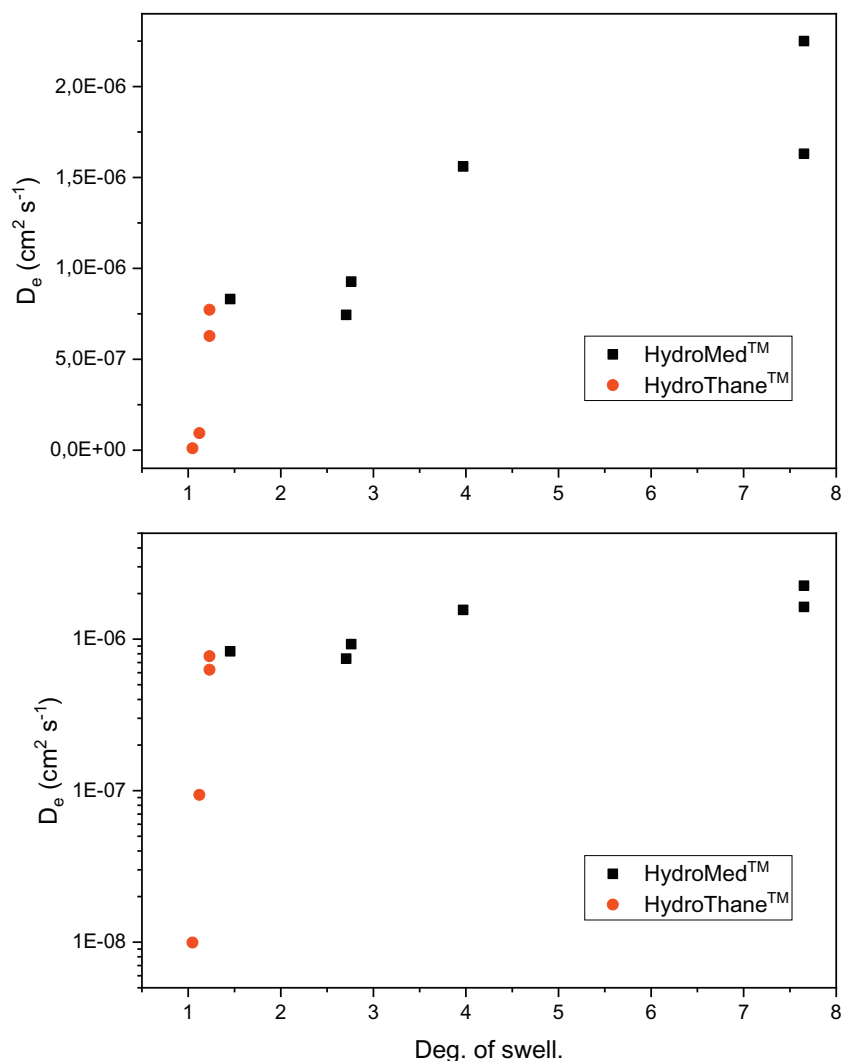

Fig. 2. Graphical illustration of effective diffusion coefficients (D_e) for a series of HydroThane™ H5 and −H25 mixed in different weight ratios. Values are reported in Table 2.

10^{-6} cm² s⁻¹, where we have measured a value of 5.76 10^{-7} cm² s⁻¹ ± 4.60 10^{-8} cm² s⁻¹. There are most likely several reasons for this difference. Two obvious options are either the difference in the tested PMMA or the different conditions used for testing. Herman et al. [38] used commercial plastics and 98% H_2O_2 for several days, whereas we have used laboratory grade PMMA and 1 M concentration. Additionally, it should be mentioned that the prepared PMMA membrane is more permeable than anticipated. We expected a fairly low permeability, because of the hydrophobicity of PMMA, but observed a somewhat higher diffusivity.

The exact composition of the tested polyurethanes is unknown to the authors. However, usually commercial polyurethanes are built of two segments, a hydrophilic part and a hydrophobic part (soft- and hard segments, respectively). Cross-linking of the chains happens because the hydrophobic parts organize in small domains, for instance by crystalizing or as a consequence of poor solubility [24]. Due to this, we investigated the effects of mixing two of the HydroThane™'s (H5 and H25) by measuring the permeability of films prepared with different weight ratios. The results can be seen in Table 2 (entry 10–15) and graphically in Fig. 2, where it is shown that the diffusivity increases in a non-linear fashion with increasing content of H25. We see this as an effect of the morphology of the polyurethanes. It is assumed that the hydrophobic parts in H5 and H25 are the same (we don't know) and that the hydrophilic parts differ. Also, the reported diffusivities are mean values assuming the uniform distribution of the two polymers in the membrane. However, this may not be the case though, so that the polymers form 'domains' of mainly H5 or H25. Then, regarding the membrane as a resistance for the flux across the membrane, where diffusion mainly occurs through channels of water, the varying polymer ratio will affect these channels. i.e., as the hydrophilic part of H25 form more water channels relative to the hydrophilic part of H5, the increasing ratio of H5 in the membrane will disrupt formation of the channels from H25. Thus, when the content of H5 decreases, the non-uniform distribution leads to larger parts of the membrane consisting of H25, and thereby prompting faster diffusion.

Fig. 3 shows impact of water content in the polymer film on the effective diffusion coefficients. It is seen that increasing water content results in higher values of permeability, and that the correlation is approximately linear. Also, there seems to be a critical degree of swelling, where the slope decreases significantly, which is even more evident on a logarithmic scale. H_2O_2 diffuses in water with an effective coefficient of approximately $1.5 \cdot 10^{-5}$ to $2 \cdot 10^{-5}$ cm² s⁻¹ [13,39], and

Fig. 3. Graphical illustration of the correlation between degree of swelling and effective diffusion coefficients (D_e) for a series of HydroMed™ (black) and HydroThane™ (red) on a linear scale (top) and logarithmic scale (bottom). Values are reported in Table 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

as the water content in the membrane decreases the effects on diffusivity is relatively prominent. Hence, the limiting factor for diffusion becomes the water content, whereas, at low levels of water in the membrane, the limiting factor becomes the polymer chains.

4. Conclusion

In summary, we have tested various commercially available polymers for hydrogen peroxide permeability. Effective diffusion coefficients are obtained from concentration evolutions of H_2O_2 in two compartments separated by a polymer membrane. Measured values are in the range of $5.12 \ 10^{-9} \pm 8.50 \ 10^{-10}$ to $2.25 \ 10^{-6} \pm 1.00 \ 10^{-7}$ for polyurethanes, $1.50 \ 10^{-6} \pm 7.00 \ 10^{-8}$ for Nafion® 117, and $5.76 \ 10^{-7} \pm 4.60 \ 10^{-8}$ for PMMA.

For the tested polyurethanes, there is a correlation between diffusivity of H_2O_2 and degree of swelling. At relatively high water content in the polymer film, the change in D_e is lower compared to relatively low deg. of swell., which is evident in Fig. 3.

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All authors attest that they meet the current ICMJE criteria for Authorship.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sbsr.2018.10.001.

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