

Advancing electrochemical measurements of the hydrogen diffusion, solubility, and permeability in polymers

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ABSTRACT

In hydrogen technologies, polymers play a key role due to their chemical corrosion-resistance and mechanical robustness. Yet, reported data characterizing hydrogen permeation in polymers are scarce. In this work, the methodology for electrochemical measurements of hydrogen permeation through polymers is improved and applied to determine the temperature dependence of hydrogen permeability, diffusion coefficient, and solubility of polypropylene, polytetrafluoroethylene, polyphenylene sulfide, polyether sulfone, and polyether ether ketone. Sputtered palladium films on the polymers act as hydrogen oxidation catalysts, while the transient oxidation current during a hydrogen pressure drop is measured. The time dependence of the measured permeation rates is fitted to numerical simulations based on Fick's second law, allowing to determine diffusion coefficients, solubilities, and permeabilities. This procedure increases precision compared to the state-of-the-art time lag method, which relies on a simplified analytical model. The observed differences in hydrogen transport are related to the structural and physicochemical properties of the polymers.

1. Introduction

The progress of the hydrogen economy is partly slowed down by high investment costs that are linked to the usage of costly corrosion resistant metals such as nickel or stainless steels for technical apparatuses [1,2]. Hydrogen embrittlement represents a critical degradation mechanism in high-strength metallic materials, caused by the dissolution and diffusion of atomic hydrogen in the metal lattice [3–7]. In contrast, polymeric materials are not susceptible to classical hydrogen embrittlement phenomena and experimental studies on semi-crystalline polymers such as polyethylene and polyamide have shown negligible influence of hydrogen on tensile properties and no deleterious long-term aging effects [8,9]. Hence, non-metallic materials may pave the way towards more robust and economically feasible technical designs for hydrogen technologies. For instance, the financial impact of electrolyzers is associated with the use of expensive metals [10,11], while their replacement with polymer-based cell components have the potential to reduce costs for the hydrogen production [12]. Moreover, polymers are discussed as physical barriers in hydrogen containers and pipelines to

slow down the hydrogen embrittlement of metals [13,14]. For such use cases the hydrogen transport in polymers displays a decisive property [15,16].

The hydrogen transport through non-convective media is typically characterized in terms of permeability (P), diffusion coefficient (D), and solubility (S) [17]:

$$P = D S. \quad (1)$$

By Fick's second law, the gas permeation through a medium can be modeled for dynamic boundary conditions such as varying pressures [18]. The diffusion and permeability of polymers are reported to decrease towards higher densities, degree of crystallinities, filler contents, and cross-linking densities [19]. These trends are associated with lower fractions of free-volumes, which provide less intermolecular space through which small molecules can move. Conversely, additives that expand the free volume (such as plasticizers or residual solvents) increase the diffusion coefficients [19,20].

In 1962, Devanathan et al. [21] presented electrochemical measurements of hydrogen permeating through a palladium foil. Hydrogen

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was generated *in-situ* by cathodic polarization, permeated through the palladium, and subsequently was electrochemically oxidized to protons on the opposite side, where the oxidation current was recorded as a function of time. Thus, the palladium foil simultaneously served as the medium for hydrogen transport and as the electrocatalyst for hydrogen oxidation. The diffusion coefficient was determined using the so-called “time-lag method,” in which the characteristic time corresponds to the point at which the permeation current reaches 63% of its steady-state value after the onset of cathodic hydrogen generation [22]. This method is motivated by an analytical solution of Fick's law for the hydrogen permeation [22]. Based on the steady-state value of the current with hydrogen feed, the permeability was determined. With thus determined diffusion coefficient and permeability, the solubility can be calculated using Eq. (1).

In the literature [23,24], Devanathan's approach was modified to measure the hydrogen permeation in polymers. Hereto, hydrogen was supplied at the front side of a polymer foil, while a porous carbon layer coated with a catalyst was pressed onto the backside (permeate side). These electrodes were made similarly to those of polymer electrolyte membrane fuel cells, using ionomer bond platinum-carbon (Pt/C) nanoparticles that catalyze the hydrogen oxidation [25–28]. The porous carbon electrode was flooded with electrolyte, allowing to oxidize hydrogen at the platinum catalyst. Like Devanathan's approach, this setup was used to determine P , D and S based on the time-dependence of the measured currents. However, hydrogen passing the polymer membrane does not instantaneously collide with catalyst particles, leading to time delays that additionally affect the measured current dynamics. Alternatively, steady-state measurements were used to solely measure the permeability [24,29], avoiding the contributions of the hydrogen permeation in the electrode to the overall dynamics measured.

In this study, the electrochemical monitoring technique is advanced by sputter-depositing a dense palladium layer directly onto the polymer foils. This palladium layer replaces the typically employed catalyst-layer-coatings for hydrogen permeation measurements of polymers, thereby eliminating the additionally measured hydrogen transport dynamics within the porous catalyst layer. The hydrogen permeation is modeled with Fick's second law, which is fitted to the time-dependence of the measured current with an iterative procedure that is based on a minimization of the mean-square-error (MSE) between the measured and modeled data. The hydrogen pressure is reduced at one side of the polymer foil, thus avoiding the delays of the typically used switching gas supply of Devanathan's approach [23,24]. By the combination of the experimental improvements and the newly introduced numerical procedures to evaluate the data, high-precise values of P , D and S of polymer foils can be determined. This technique was applied to polypropylene (PP), polytetrafluoroethylene (PTFE), polyphenylene sulfide (PPS), polyether sulfone (PES) and polyether ether ketone (PEEK) foils in a temperature range from 30 to 80 °C. The measured data are correlated with structural properties of the polymers, showing that straightforward correlations are unreliable for single structural parameters without deeper mechanistic insight.

2. Methods

2.1. Materials and sample preparation

The polymer foils examined in this study are commercially purchased, including polyether ether ketone (PEEK) with thicknesses of 0.025 mm (RCT®-GDF-EK, RCT Reichelt Chemietechnik GmbH) and 0.1 mm (Goodfellow), polyphenylene sulfide (PPS) with a thickness 0.1 mm (Goodfellow), polyether sulfone (PES) with a thickness 0.25 mm (RCT®-GDF-SU/250 from RCT Reichelt Chemietechnik GmbH), polytetrafluoroethylene (PTFE) with a thickness 0.25 mm (Bola), polypropylene (PP) with a thickness of 0.04 mm (RCT-GDF-PP from RCT Reichelt Chemietechnik GmbH), and PP with thicknesses of 0.5 and 1 mm (RCT-SH from RCT Reichelt Chemietechnik GmbH). Palladium

films with a thickness of 550 nm are directly sputtered onto the polymer substrates by physical vapor deposition (PVD) using a Q150 V ES Plus by Quorum with a 57 mm palladium target (MaTeck GmbH). This palladium layer acts as a hydrogen oxidation catalyst, while it affects the total permeation measured insignificantly due to its high diffusion coefficient of $1.04 \times 10^{-5} \text{ cm}^2/\text{s}$ at 60 °C [30] in combination with its thin thickness. The thickness of 550 nm of the palladium layer was the thinnest configuration that achieved mechanical stability and a continuous pinhole-free coating of the polymer foil (see electronic supplementary information (ESI) Section S1). Prior to sputter deposition of palladium, all polymer films are roughened with 4000-grit sandpaper and cleaned with isopropanol to improve the adhesion of the palladium film.

2.2. Experimental setup

The experimental setup used in this study is similar to that reported in Ref. [29], with the detailed description of the cell given in the ESI Section S2. In brief, the cell consists of a gas compartment and an electrolyte compartment that were separated by the examined polymer foil. In this setup, hydrogen permeates through an area of $42 \text{ mm} \times 32 \text{ mm}$ of the polymer foils, confined with flat ethylene propylene diene monomer (EPDM) rubber sealings. The backsides of the polymer foils were mechanically supported by hydrophilic carbon fleeces (E20 Freudenberg, non-PTFE containing), a platinum gauze (0.65 mm thick), and an in-house manufactured perforated PEEK sheet for mechanical support. All the parts at the backside were flooded with 1 M NaOH (SigmaAldrich suprapure NaOH pellets dissolved in Milli-Q water). The platinum gauze is welded to a platinum wire, allowing to contact the palladium layer over the carbon fleece from the cell exterior. Hence, the palladium layer could be used as the working electrode. A potentiostat (Zahner Zennium Pro) connects the working electrode to a platinum wire counter electrode, which is placed in a nitrogen-purged (100 ml/min) electrolyte compartment behind the perforated PEEK sheet. By purging with nitrogen, the hydrogen evolved at the counter electrode is carried out of the cell, minimizing its back-diffusion to the working electrode. A voltage of 0.8 V was applied between the working and counter electrode.

For the measurements, first, the cell is purged with nitrogen to reduce the amount of dissolved oxygen. After 10 min of purging, the bypass current is determined, which is subsequently subtracted from the measured hydrogen permeation current (details in Section S3 of the ESI). These bypass currents are related to mostly remaining oxygen impurities and corrosion of the carbon fleeces. Afterwards, the cell is flushed with dry hydrogen at a flow rate of 50 mL/min through a flow field pressed against the polymer films under investigation. During the measurement procedure, the hydrogen pressure started at 2.5 bar for 20 min to reach a steady permeation current. Subsequently, the pressure was released to ambient conditions by opening a valve. The moment in which the valve is opened, and the feed side pressure drops is defined as $t = 0 \text{ s}$. The feed-side pressure and the valve state were recorded simultaneously with the permeation current at an average sampling interval of approximately 0.30 s. Steady-state conditions at 2.5 bar were used to determine the permeability from the mean current density between $t = -90 \text{ s}$ and $t = -1 \text{ s}$ (see ESI Eq. S(5)). Afterwards, the current is recorded for 450 s. Measurements are repeated in 10 °C increments over the 30–80 °C range. Four measurements are taken for every temperature applied, with the first measurement being discarded.

2.3. Data evaluation

A numerical one-dimensional diffusion model was used to simulate time-dependent permeation currents. Hereto, Fick's second law was implemented using an explicit forward-time and centered-space scheme. The model was used for two configurations: (i) a one-layer film of thickness d with constant diffusivity D and solubility S representing the polymer foil only. (ii) a two-layer model representing the polymer foil

(left side, denoted by l) and the sputtered palladium layer (right side, denoted by r), that are parameterized by individual thicknesses (d_l, d_r), diffusion coefficients (D_l, D_r), solubilities (S_l, S_r), and thus permeabilities (P_l, P_r). At the interface between both media ($x = d_l$), hydrogen transport was described using an effective interfacial permeability. The interfacial permeability P_{inter} was set to 1×10^{-10} mol/cm/s/bar, corresponding to the largest numerically stable value within the chosen discretization. This value is approximately one order of magnitude larger than the permeability of the palladium layer and two orders of magnitude larger than that of the investigated polymers, ensuring that the interface does not significantly affect hydrogen transport. An analysis is provided in the ESI Section S4. The boundary conditions imply $c(0, t) = S_l p(t)$ at the feed face, where $p(t)$ undergoes a pressure decrease $p_1 \rightarrow p_2$, while at the side of the palladium layer that faces the electrolyte ($x = d$) a negligible pressure was assumed, corresponding to an instantaneous electrochemical oxidation of hydrogen. The feed-side pressure was recorded simultaneously with the permeation current at an average sampling interval of approximately 0.30 s. The mean measured pressure before valve opening, (p_1), and the mean final pressure, (p_2), were used as the initial and final feed-side boundary pressures in the numerical model. The time origin was defined by the recorded transition of the pressure-release valve from the closed to the open state. The pressure decrease occurred within less than approximately 0.4 s and was therefore represented by only one or two acquisition intervals, which did not permit reliable reconstruction of its detailed temporal profile. In comparison, the shortest permeation-current transient was approximately 80 s, defined as the time required for the current to complete 95% of the change between its initial and final steady-state values. The pressure-release duration thus represented less than 0.5% of the shortest measured transient. Accordingly, only the temporally unresolved transition between the measured pressure levels was approximated as an instantaneous step, while the experimentally determined initial and final pressures were explicitly incorporated into the boundary conditions. An example pressure drop measurement can be found in the ESI section S12. The molar flux $\phi(t)$ of hydrogen through the polymer foil is converted to the electrochemical current density by Faraday's law

$$j(t) = zF\phi(t), \quad (2)$$

where F denotes Faraday's constant and z is the number of electrons per molecule ($z = 2$ for the hydrogen oxidation). A detailed description of the model is given in the ESI Section S5.

In Fig. 1, the transient permeation responses of the one- and two-layer models are compared. The simulations were performed using

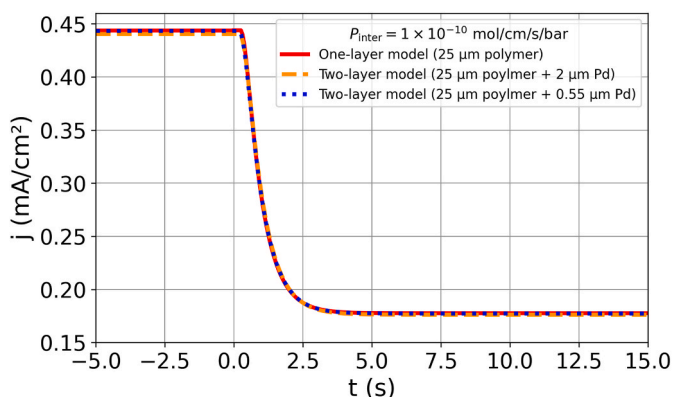


Fig. 1. Comparison of the simulated transient permeation responses obtained with the one-layer and two-layer diffusion models. Hereto, a polymer foil thickness of 25 μm was chosen, while thicknesses of the palladium layer was parameterized with 0.55 μm and 2 μm . At $t = 0$, a hydrogen partial pressure drop from 2.5 bar to 1 bar was incorporated into the model. The interfacial permeability P_{inter} was set to 1×10^{-10} mol/cm/s/bar.

input parameters of $P_l = 2.0 \times 10^{-12}$ mol/cm/s/bar, $D_l = 8.0 \times 10^{-7}$ cm²/s, and $S_l = 2.5 \times 10^{-6}$ mol/cm³/bar (similar values as that of high-performance polymers), while $P_r = 2.0 \times 10^{-11}$ mol/cm/s/bar, $D_r = 1.0 \times 10^{-6}$ cm²/s, and $S_r = 2.0 \times 10^{-5}$ mol/cm³/bar were used for the palladium layer based on literature values [31,32].

For a Pd thickness of 0.55 μm , the two-layer model is virtually indistinguishable from the single-layer prediction, with only negligible deviations, resulting in a mean square error of 6.00×10^{-7} mA²/cm⁴. Increasing the palladium thickness to 2.0 μm leads to a slightly higher deviation between the models, reflected by an increased mean square error of 2.58×10^{-6} mA²/cm⁴. Based on this comparison, the used palladium layer thickness of 0.55 μm is estimated to insignificantly effect the permeation dynamics, for which the following data evaluation were conducted with the single-layer model.

2.4. Fitting procedure

Fig. 2 summarizes the workflow used to extract the hydrogen diffusion coefficient D and solubility S from the transient permeation experiments. Hereto, the measured current density transient $j(t)$, the experimentally determined permeability P from steady-state current before the pressure decrease (see ESI Eq. S(5)), and the membrane thickness were used as input parameters. The fitting procedure starts by defining a wide initial search interval for D . Within each iteration, 50 diffusion coefficients are evaluated on a logarithmic grid. For each of those values of D , the corresponding solubility is calculated from the relation $S = P/D$. Using the parameter pair of D and S , the transient current response is numerically simulated and compared with the experimental transient. The agreement with the experimental data is quantified by calculating the mean squared error (MSE) according to

$$MSE = \frac{1}{n} \sum_{i=1}^n (j_i - \hat{j}_i)^2, \quad (3)$$

where j_i is the measured current density and $\hat{j}_i$ is the simulated current density at time t . Prior to the MSE evaluation, both datasets are interpolated onto a common time basis to enable a pointwise comparison.

The diffusion coefficient yielding the smallest MSE was selected as the best candidate of the iteration. To refine the parameter search, the diffusion coefficient interval for the subsequent iteration was restricted to the two neighboring grid points surrounding this optimal value on the logarithmic grid. Specifically, if the minimum MSE occurred at grid index k , the new lower and upper bounds of the search interval were defined by the diffusion coefficients at indices $k - 1$ and $k + 1$. If the minimum occurred at the lower or upper boundary of the grid, the refined interval was defined by the first two or last two grid points, respectively. This procedure ensures that the search interval always remains within the predefined parameter space evaluated by the model while systematically increasing the resolution around the most probable diffusion coefficient. The grid-refinement procedure was repeated for a minimum of three times to ensure sufficient refinement, while it was restricted to a maximum of five iterations to limit computational effort. Convergence was assumed when the improvement in the MSE between successive iterations fell below a predefined threshold of 1×10^{-8} mA²/cm⁴. Thus, the best fit of the numerical model to the experimental data was obtained, yielding the fitted values for D and S . The robustness of the fitting procedure with respect to the logarithmic grid density, maximum number of refinement iterations, and MSE convergence tolerance was verified using three representative measurements covering the investigated diffusion range (ESI Section S11).

Fig. 3 shows an example of the data evaluation using one measurement of PES at 40 $^{\circ}\text{C}$. The simulation with a diffusion coefficient of 8.19×10^{-7} cm²/s demonstrates the best fit of this iteration to the measured data. Only a small number of individual data points of the experiments deviate noticeably from the general trend. These sporadic

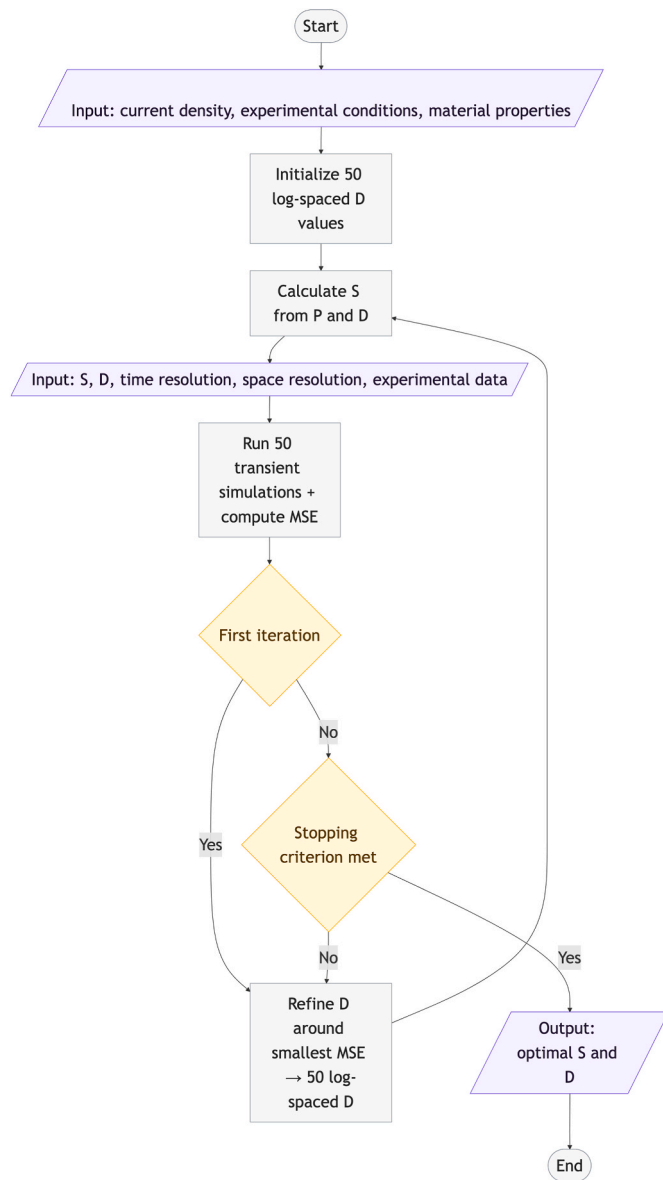


Fig. 2. Workflow of the iterative parameter-extraction procedure used to determine the hydrogen solubility S and diffusion coefficient D from transient permeation experiments. Starting from the experimental inputs (current density, experimental conditions, and material properties), a wide initial range of diffusion coefficients is defined. Solubility is calculated from permeability and diffusion, followed by transient numerical simulations. The agreement between simulated and experimental current transients is quantified using the mean squared error (MSE). Based on the MSE minimum, the diffusion-coefficient range is iteratively refined until a stopping criterion (five iterations or $MSE < \times 10^{-8} \text{ mA}^2/\text{cm}^4$) is met, yielding the optimal values of S and D .

deviations do not exhibit systematic behavior and are attributed to short-term electrochemical fluctuations, such as the above discussed back-diffusion of hydrogen bubbles from the counter electrode to the working electrode (see Section 2.2). For the purpose of the visual demonstration, only 10 of the total 50 iterations used for the variation of the diffusion coefficient in the model are displayed in this example. At time $t = 0$, the hydrogen partial pressure was lowered from 2.5 bar to ambient pressure. As previously outlined, the fitting procedure is repeated using a finer variation range of the diffusion coefficient until the convergence ($MSE < 10^{-5} \text{ mA}^2/\text{cm}^4$) is reached.

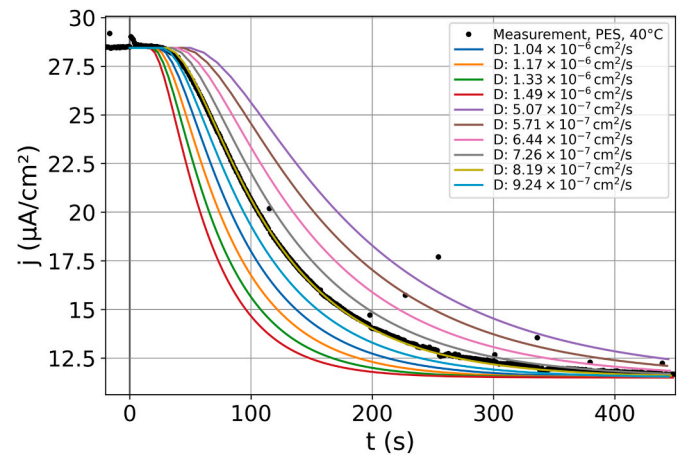


Fig. 3. Example measurement with comparison of 10 simulations with measurement of PES at 40 °C. The measurement data shown were down sampled by block averaging, with two consecutive samples grouped into non-overlapping blocks and replaced by their mean values (block size = 2).

2.5. Exponential fits

The temperature dependence of hydrogen diffusion in polymers is approximated by an Arrhenius-type relationship, reflecting the thermally activated nature of the hydrogen diffusion through polymer chains [19].

$$D = D_0 \cdot \exp\left(-\frac{E_D}{RT}\right), \quad (4)$$

where D_0 displays the pre-exponential factor, R the ideal gas constant, T the temperature, and E_D the activation energy. Analogously, the temperature dependence of permeability and gas solubility is approximated:

$$P = P_0 \cdot \exp\left(-\frac{E_P}{RT}\right), \quad (5)$$

$$S = S_0 \cdot \exp\left(-\frac{\Delta H_S}{RT}\right), \quad (6)$$

where E_P denotes the activation energy of permeation and ΔH_S the enthalpy of solution.

For each material and temperature, the mean values and sample standard deviations of D , P , and S were calculated from the independent repeat measurements. The sample standard deviations were used to represent experimental repeatability. The temperature-dependent parameters were obtained by weighted linear least-squares regression of $\ln(X)$ against $1/T$. To account for residual scatter not captured by the repeatability error bars, the covariance matrix of each fit was scaled by the corresponding reduced chi-square. The scaled covariance matrices were used to calculate the standard errors, 95% confidence intervals of E_D , E_P and ΔH_S , and pointwise 95% confidence bands of the fitted relationships. A detailed description of the statistical uncertainty analysis is provided in Section S13 of the ESI.

3. Results & discussion

3.1. Measurement reproducibility and accuracy

Fig. 4 shows current transients for PEEK (A–C) and PES (D–F) foils at 30, 50, and 80 °C during a pressure drop from 2.5 to 1 bar hydrogen pressure at the front side. A comparison measurement with a Pt/C gas diffusion electrode instead of a sputtered Pd layer can be found in the ESI section S6. Each combination is represented by three measurements to show the reproducibility. In addition, the best fit of the simulation to the

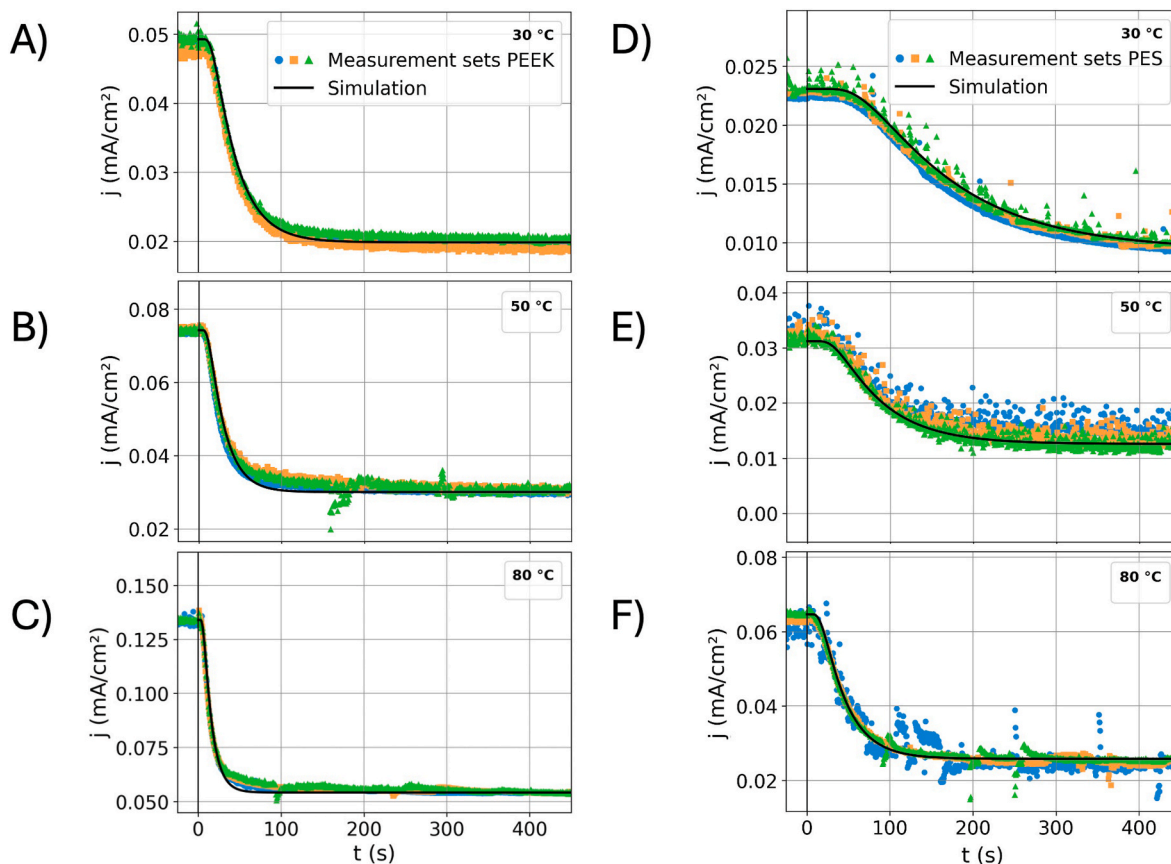


Fig. 4. Measurement reproducibility and accuracy for hydrogen permeation experiments performed with PEEK (125 μm) and PES (250 μm) membranes. A) PEEK at 30 $^{\circ}\text{C}$, B) PEEK at 50 $^{\circ}\text{C}$, C) PEEK at 80 $^{\circ}\text{C}$, D) PES at 30 $^{\circ}\text{C}$, E) PES at 50 $^{\circ}\text{C}$, F) PES at 80 $^{\circ}\text{C}$. For each temperature, three independent measurements were displayed to assess the reproducibility. Experimental data are shown for all repetitions, while numerical simulations are presented only for the measurement highlighted in green. The measurement data shown were down sampled by block averaging, with two consecutive samples grouped into non-overlapping blocks and replaced by their mean values (block size = 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

experimental data is shown based on the approach discussed in Section 2.4. The complete dataset of all examined polymers (PEEK, PES, PPS, PTFE, and PP), consisting of measurements in 10 $^{\circ}\text{C}$ increments over the full temperature range from 30 to 80 $^{\circ}\text{C}$ can be found in the ESI Section S10. For PEEK, the gap between steady-state current levels before and after the pressure drop decreases towards higher temperatures. Thus, the sensitivity of the transient response to small deviations increases, causing higher uncertainties in the measured current. When directly comparing PEEK and PES, PES shows a better agreement between measurement and simulation, which may be related to the different membrane thicknesses (PEEK: 125 μm ; PES: 250 μm) and the resulting overall lower current levels for PES and the larger time until the steady state is reached after the pressure drop. On the contrary, towards thinner polymer foils the diffusion rates through the polymer foils increase and the more likely the low-surface area palladium layer can run into a catalytic saturation of the hydrogen oxidation. Further details on the influence of foil thickness, including plots of all measurements and additional comparisons of the *MSE* as a function of temperature, are provided in Section S9 of the ESI.

The reproducibility of the extracted diffusion coefficients was assessed from three independent measurements per temperature using the variation-factor (f_{var}), which is here defined as the ratio of the standard deviation (σ_D) to the mean diffusion coefficient ($\bar{D}$):

$$f_{\text{var}} = \frac{\sigma_D}{\bar{D}} \quad (13)$$

For PEEK, the lowest f_{var} of 0.67% was observed at 30 $^{\circ}\text{C}$, whereas at 50 $^{\circ}\text{C}$ it increased to 6.84%, suggesting increased sensitivity of the

extracted diffusion coefficients to experimental fluctuations at intermediate temperatures. For PES, f_{var} showed values of 2.40% at 30 $^{\circ}\text{C}$, 4.34% at 50 $^{\circ}\text{C}$, and 4.03% at 80 $^{\circ}\text{C}$. For all investigated materials and temperatures, the f_{var} values were below 7%, demonstrating good reproducibility of the applied measurement and evaluation procedure.

3.2. Comparison of polymers and temperature dependence

In Fig. 5, the values of the permeability P , diffusion coefficient D , and solubility S for all examined polymers are shown in the temperature range from 30 to 80 $^{\circ}\text{C}$. The complete datasets are provided in Table S1 of the ESI. The hydrogen permeability spans more than one order of magnitude across all investigated polymers, covering values from 7.6×10^{-13} to 1.61×10^{-11} mol/cm/s/bar. PP consistently exhibits the highest permeabilities, increasing from 2.64×10^{-12} mol/cm/s/bar at 30 $^{\circ}\text{C}$ to 1.61×10^{-11} mol/cm/s/bar at 80 $^{\circ}\text{C}$. In contrast, the high-performance polymers PEEK, PES, PPS, and PTFE show permeabilities predominantly in the range of $(0.76 - 3.89) \times 10^{-12}$ mol/cm/s/bar within the entire temperature window considered. Hence, PP exhibits permeabilities that are approximately five to ten-times higher than those of the high-performance polymers.

Similar to the permeabilities, PP exhibits diffusion coefficients that are typically five to ten times higher than those of the high-performance polymers with respect to the same temperatures. The high-performance polymers show similar values of the diffusion coefficients. In contrast to the significant temperature dependence of the diffusion coefficient, the hydrogen solubilities are less affected by temperature and even material, showing values between 0.95×10^{-6} and 3.14×10^{-6} mol/cm³/bar.

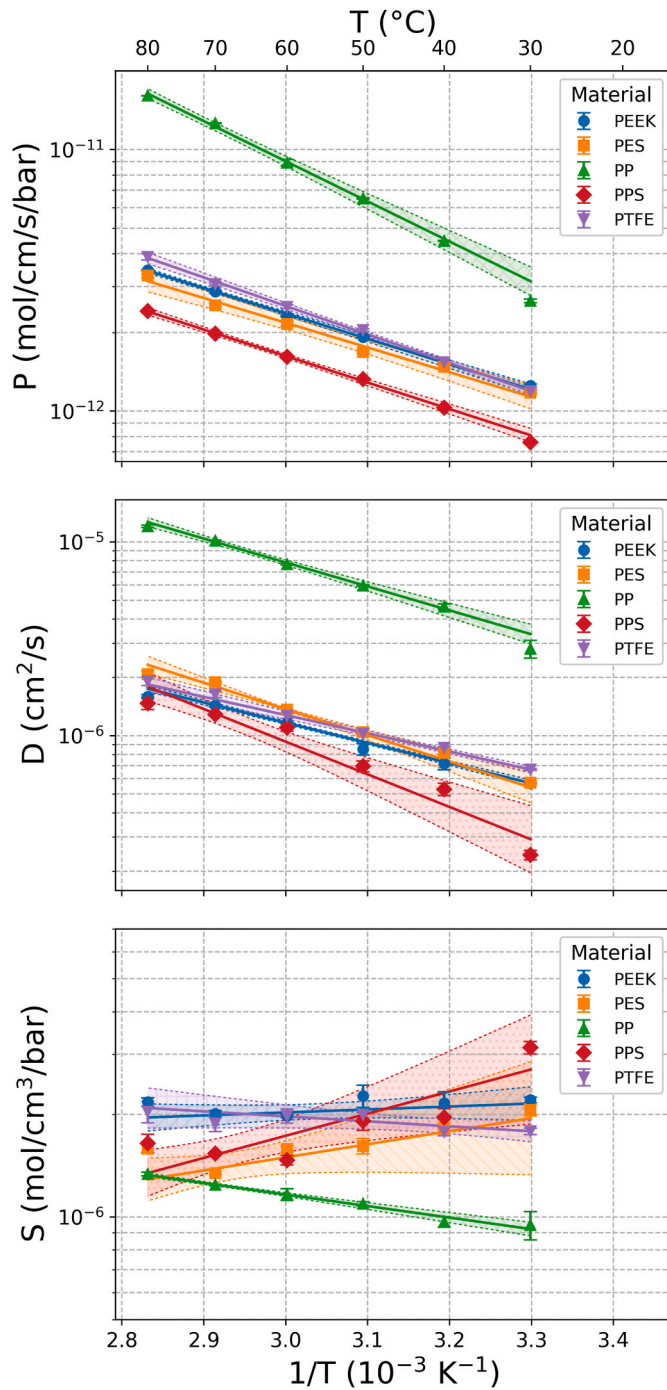


Fig. 5. Arrhenius plots of the measured permeation, diffusion coefficient, and solubility of hydrogen. The symbols represent the mean values of the independent measurements, while error bars indicate their sample standard deviations. Solid lines show weighted linear regressions of $\ln(S)$ against $1/T$. The shaded and hatched regions represent pointwise 95% confidence bands calculated from the covariance matrix scaled by the reduced chi-square. The confidence intervals were determined using Student's t distribution with four degrees of freedom.

Exponential fits of Arrhenius law (Eqs. (4)–(6)) were applied to parameterize the observed temperature dependencies of P , D , and S as summarized in Table 1. The activation energies for diffusion $E_{a,D}$ range from 18 kJ/mol for PTFE to 32.3 kJ/mol of PPS. The enthalpies of solution ΔH_S are comparatively small in magnitude and exhibit both positive and negative values in the range of -12.4 to 6.48 kJ/mol.

The uncertainties of the fitted parameters were evaluated by

weighted linear regression of $\ln(S)$ against $1/T$, using the standard deviations of the independent repeat measurements as statistical weights. The fit covariance matrices were scaled by the corresponding reduced chi-square, and 95% confidence intervals were calculated using Student's t -distribution. The complete uncertainty results are provided in Table S3 of the ESI. For PEEK and PES, the 95% confidence intervals of ΔH_S include zero. Their negative point estimates are therefore not statistically distinguishable from a temperature-independent solubility within the investigated temperature range. In contrast, the 95% confidence interval obtained for PPS remains entirely negative. Nevertheless, the results obtained with PPS should also be interpreted cautiously as the elevated reduced chi-square indicates residual scatter that is not fully described by the error bars. The relation between the structural properties of the different polymers and their effect on the measured hydrogen permeation properties are discussed below (see Section 3.4), after the experimental data is compared to literature values.

3.3. Comparison to literature data

Table 2 summarizes literature [33,34] values of P , D , and S for PTFE and PEEK with lowest crystallinity and compares them to the data of this study. Overall, the relative deviations range between -6% and -26% , which can plausibly be attributed to differences in crystallinity, morphology, and thermal history of the investigated samples. Hence, the observed agreement supports the validity of the applied methodology.

3.4. Impact of the polymer structures on the hydrogen transport

The following discussion aims to relate the thus far presented differences of the hydrogen transport through the different polymers to their structure. For this purpose, Table 3 shows some of the physico-chemical properties of the polymers, such as their density, melting point, glass-transition temperature, fraction of hydrogen atoms, and the atomic molar density. The fraction of hydrogen atoms f_H was calculated as the ratio of the number of hydrogen atoms N_H to the total number of atoms N_{total} in the chemical repeat unit:

$$f_H = \frac{N_H}{N_{\text{total}}} \quad (14)$$

In addition, the atomic molar density was calculated by

$$\rho_{\text{atoms}} = \frac{\rho}{M_{\text{RU}}} \cdot N_{\text{total}}, \quad (15)$$

where ρ represents the polymer density and M_{RU} the molar mass of the repeat unit.

Fig. 5 shows an outstandingly high hydrogen permeability of PP, while it shows in Table 3 with just 0.9 g/cm^3 the by far lowest density. In contrast, PTFE shows almost twice the density of PPS, PES, and PEEK, yet they all these polymers show similar hydrogen permeabilities. Hence, the differences in the density alone cannot explain the different hydrogen transport properties observed.

PTFE, PPS, and PEEK show melting points in a relatively narrow range between 285 and 343 °C, which are significantly higher than that of PP at 130 °C. Hence, the trend of the measured hydrogen permeabilities is partly reflected by the melting points. The glass transition temperature of PP in the range between -30 and -20 °C is also significantly lower than that of PTFE, PPS, and PEEK, which range between 93 and 143 °C, whereas PES shows an outstandingly high glass transition temperature of 228 °C. The glass transition temperature and melting temperature both reflect mobilities and intramolecular forces between the monomers in the polymer, which are also expected to affect the thermally activated hydrogen hopping through the tangled monomers [40,41]. Hence, to a certain degree, the thermochemical and thermo-mechanical properties and the hydrogen permeability are expected to correlate.

Table 1

Pre-exponential factors and activation energies of PEEK, PES, PP, PPS and PTFE in the temperature range of 30–80 °C.

Material	$D_0 \pm \sigma(D_0)$ ($\times 10^{-4}$ cm ² /s)	$E_{a,D} \pm \sigma(E_{a,D})$ (kJ/mol)	$P_0 \pm \sigma(P_0)$ ($\times 10^{-9}$ mol/cm/s/bar)	$E_{a,P} \pm \sigma(E_{a,P})$ (kJ/mol)	$S_0 \pm \sigma(S_0)$ ($\times 10^{-6}$ mol/cm ³ /bar)	$\Delta H_S \pm \sigma(\Delta H_S)$ (kJ/mol)
PEEK	15.8 ± 1.14	20 ± 0.20	1.93 ± 0.13	18.6 ± 0.19	1.11 ± 0.19	−1.67 ± 0.48
PES	159 ± 25.41	25.9 ± 0.44	1.5 ± 0.19	18.1 ± 0.34	0.105 ± 0.02	−7.36 ± 0.66
PP	400 ± 54.48	23.7 ± 0.38	364 ± 10.78	29.4 ± 0.08	12.1 ± 2.09	6.48 ± 0.49
PPS	1060 ± 381.46	32.3 ± 1.01	1.78 ± 0.11	19.4 ± 0.17	0.0194 ± 0.01	−12.4 ± 0.80
PTFE	8.46 ± 1.48	18 ± 0.46	4.68 ± 0.65	20.9 ± 0.37	5.4 ± 1.64	2.79 ± 0.80

Table 2

Comparison of P, D and S data at 25 °C calculated from the Arrhenius-fits of this study and that of literature values. a) Calculated from the pre-exponential factors and activation energies reported in this paper. b) The sample with the lowest crystallinity was chosen from the reference.

Material	Ref.	P (10^{-12} mol/cm/s/bar)	D (10^{-7} cm ² /s)	S (10^{-7} mol/cm ³ /bar)
PTFE ^a	This Study	1.04	5.93	17.50
PTFE Rel. Deviation	[33]	1.33 −21.8%	8.03 −26.2%	16.20 8.0%
PEEK ^a	This Study	1.07	4.98	21.75
PEEK ^b Rel. Error	[34]	1.26 −15%	5.32 −6.4%	23.70 −8.2%

Table 3 shows that PP has the highest atomic molar density (0.193 mol atoms/cm³) among the investigated polymers. This closest atomic packing may be a hurdle for the hydrogen permeation and at least compensate for some of the previously discussed factors that lead to a high permeability. However, PP also shows the highest hydrogen atom fraction (66.7%). The high hydrogen fraction reflects the aliphatic and lightweight backbone of PP, which shows higher flexibility and comparatively weak intermolecular interactions compared to aromatic polymer systems such as PES, PPS, and PEEK. Hence, the highest atomic molar density of PP does not contradict its comparatively high hydrogen diffusivity, as atomic packing density represents a static descriptor and does not capture the dynamic rearrangement capability of the polymer matrix. With more rigid polymer structures caused by bulky repeat units and strong intermolecular interactions, segmental motions and transient free-volume formation are suppressed, even at comparable or lower atomic molar densities. In the case of PTFE, the tangled monomers are less stiff and more flexible than in the case of PES, PPS, and PEEK, which is for instance observable PTFEs tendency for mechanical creep under applied pressure. However, the high mass of PTFE and the sluggishness it causes partly compensate for the weaker stiffness compared to PES, PPS, and PEEK, so that these polymers end up with a similar hydrogen permeability.

To conclude, the process of hydrogen permeation in polymers is related to an interplay of many of the physicochemical and structural properties that are summarized by the measures stated in Table 3. However, the hydrogen permeation is affected by the dynamic rearrangement and thermal oscillations of the polymer structure, which are

not directly described by the measures of Table 3. Molecular dynamics (MD) simulations [42,43] describe gas diffusion in polymers as a hopping process between transient microcavities governed by cooperative segmental motions of the surrounding polymer chains. Penetrant molecules oscillate within local free-volume elements and execute rapid jumps into neighboring cavities only when sufficient transient free volume becomes available. Both the frequency of these hopping events and the characteristic jump lengths decrease with increasing chain rigidity and steric constraints [42]. In particular, the MD study by Takeuchi et al. [43] demonstrates that the temperature dependence of the simulated diffusion coefficients follows an Arrhenius-type behavior, which was also observed in this study. The simulations further revealed that the distribution and temporal fluctuations of free volume, governed by segmental dynamics, significantly influence both the magnitude of diffusion coefficients and the associated activation barriers [43]. Consequently, differences in hydrogen diffusivity among the investigated polymers cannot be fully captured by static descriptors such as density, atomic molar density, or glass-transition temperature alone, but rather reflect some interconnections to the dynamic behavior of the polymer matrix arising from the combined effects of chemical structure, segmental mobility, and morphology.

Fig. 5 showed that the solubilities of the investigated polymers are slightly affected by temperature. Hence, owing to these small changes of the values with temperature, the extracted enthalpies of solution are highly affected by even small uncertainties in the data evaluation. The uncertainty analysis shows that the negative values obtained for PEEK and PES are not statistically distinguishable from zero because their 95% confidence intervals include both negative and positive values. Therefore, these results do not provide conclusive evidence of negative solution enthalpies for PEEK and PES. For PPS, however, the 95% confidence interval remains entirely negative. The negative ΔH_S obtained for PPS can therefore not be attributed solely to the statistical variation observed among the repeat measurements. Nevertheless, its magnitude should be interpreted cautiously because the elevated reduced chi-square suggests additional residual scatter, possible systematic uncertainty, or deviations from the simplified Arrhenius-type description. Negative enthalpies of solution have also been reported for the dissolution of CO₂, O₂, and N₂ in PTFE [33,44]. This behavior has been interpreted as a condensation-like process with minimal specific interactions between gas molecules and the polymer matrix. Like the hydrogen diffusion, the hydrogen solubility is affected by the temperature induced dynamics of the chain vibrations and thus displays a very complex property to understand and model. To conclude, this discussion aims to highlight that the influence of structural polymer properties on the hydrogen

Table 3

Repeat units and selected physicochemical properties of the investigated polymers, including density, melting point, glass-transition temperature, hydrogen atom fraction within the repeat unit, and atomic molar density [35–39].

Material	Repeat unit	Density (g/cm ³)	Melting point (°C)	Glass-transition temperature (°C)	f_H (%)	ρ_{atoms} (mol atoms/cm ³)
PP	C ₃ H ₆	0.90	130	−30 to −20	66.7	0.193
PTFE	C ₂ F ₄	2.20	327	120 to 130	-	0.132
PPS	C ₆ H ₄ S	1.35	285	93	36.4	0.137
PES	C ₁₂ H ₁₀ O ₄ S	1.37	-	228	37.0	0.148
PEEK	C ₁₉ H ₁₂ O ₃	1.32	343	143	35.3	0.156

permeation is a complex topic that requires advanced models for a detailed understanding.

4. Conclusion

In this study, the electrochemical measurement technique to determine hydrogen diffusion coefficients, permeabilities, and solubilities of polymer foils was experimentally improved by introducing a sputtered palladium layer as an electrocatalyst and a pressure drop procedure. Both experimental innovations reduced measurement errors that affected the hydrogen transport dynamics in previous studies. Moreover, the data evaluation procedure was advanced with an iterative fitting procedure that uses a numerical simulation based on Fick's second law, allowing the precise simulation of the measured current transients of the hydrogen permeation through the examined polymer foils. This procedure was applied to determine the hydrogen transport properties of PP, PTFE, PPS, PES, and PEEK foils in the temperature range from 30 to 80 °C. PP showed an approximately five-times higher hydrogen permeability and diffusion coefficient than those of the investigated high-performance polymers (PTFE, PPS, PES, and PEEK). These differences were attributed to a combination of structural and physicochemical factors, including higher monomer rigidity, higher sluggishness of the more heavyweight monomers, stronger intermolecular interactions, elevated glass transition temperatures, and so forth. Importantly, no single structural descriptor was discussed as sufficient to fully explain

the observed transport behavior, underscoring the multifactorial and dynamic nature of hydrogen transport in polymers.

CRedit authorship contribution statement

Laurin Dohlen Hensen: Writing – original draft, Visualization, Software, Methodology, Investigation, Conceptualization. **Maximilian Schalenbach:** Writing – original draft, Visualization, Supervision, Software, Methodology, Funding acquisition, Conceptualization. **Hermann Tempel:** Writing – review & editing, Project administration, Funding acquisition. **Rüdiger-A. Eichel:** Project administration, Funding acquisition.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abbreviations

MSE	Mean Square Error
Pd	Palladium
PEEK	Polyether ether ketone
PES	Polyether sulfone
PP	Polypropylene
PPS	Polyphenylene sulfide
PTFE	Polytetrafluoroethylene
PVD	Physical Vapor Deposition

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2026.157189>.

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