Porosimetry by Means of Positron Annihilation

R. Krause-Rehberg, Dept. of Physics, University Halle
**Positron Annihilation Lifetime Spectroscopy - PALS**

When trapped in vacancies:
- Lifetime increases due to smaller electron density in open volume

**positrons:**
- thermalize (reach thermal energies)
- diffuse
- being trapped
- and annihilate

**When trapped in vacancies:**
- Lifetime increases due to smaller electron density in open volume
Digital lifetime measurement

- much simpler setup
- timing very accurate
- pulse-shape discrimination (suppress “bad pulses“)
- each detector for start & stop (double statistics)
Screenshot of two digitized anode pulses

Fullscale: 1, Offset: 0.45, results in [240.976, -12.6819], ymax: 0.56375, dy: -253.659

Zero line: 0.0420833

Fraction Point: -0.127199

Minimum at: 41.4432

Fraction Point At: 27.5605

Minimum: -0.522192

Fullscale: 1, Offset: 0.45, results in [312.411, 16.4417], ymax: 0.434644, dy: -328.854

Zero line: 0.0379167

Fraction Point: -0.0921488

Minimum at: 33.9069

Fraction Point At: 40.0176

Minimum: -0.395635

Time difference = 2.65471 samples = 663.67 ps
Hamamatsu PMTs H-3370 are combined with plastic scintillators EJ-232. The anode pulses are digitized by Aqciris DC211, DC252 or DC282 digitizers. All PMT’s act as start and stop detectors, thus 2, 6 or 12 spectra are collected with 2, 3 or 4 PMT’s simultaneously.
The complete spectrometer.
In materials without free electrons Positronium may be formed (Polymers, glass, liquids, gases).
Principles of PALS: pick-off Annihilation

pick-off annihilation:

- $o$-Ps is converted to $p$-Ps by capturing an electron with anti-parallel spin
- Happens during collisions at walls of pore
- Lifetime decreases rapidly
- Lifetime is function of pore size 0.5 ns ... 142 ns
- Lifetime can be extracted from spectra
Principles of PALS: typical spectrum

For porous glass:

- 4 exponential decay components
- p-Ps $\rightarrow 0.125$ ns
- Free positrons $\sim 0.5$ ns
- o-Ps in amorphous region of glass $\sim 1.5$ ns
- o-Ps in pores

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$
Principles of PALS: typical lifetimes

- Metals and alloys
- V, V₂, V₆t₃, VX
- Semi-conductors
- Polymers
- Mesoporous materials
  - low-K dielectrics
  - Zeolites
  - Silica gels
- Porous glasses

Lifetime (ns)

- 0 ns
- 0.1
- 1
- 10
- 100
- 142 ns
PALS: detection limits

- lower detection limit: open volume of 3Å diameter
- e.g. open volume between polymer chains

- upper limit: 60 nm diameter
- physical limit: vacuum lifetime of o-Ps = 142 ns
- upper limit depends also on corresponding intensity
New Analysis Technique: MELT

MELT\(^1\) = Maximum Entropy for Lifetime Analysis

- number of components must not be known
- output is intensity versus lifetime
- pore size distribution can be determined
- disadvantage: very high statistics necessary (\(> 10^7\) counts)

\(^1\)A. Shukla et al., 1997, Materials Science Forum, 255-257, 233

porous polymer
The TE model

- Annihilation rate: \[ \frac{1}{\tau_{o-Ps}} = \lambda_{o-Ps} \]
  \[ = \lambda_{2\gamma} + \lambda_{3\gamma} \]
  \[ = \lambda_{2\gamma}^0 (P) + \lambda_{3\gamma}^0 (1 - P) \approx \lambda_{2\gamma}^0 (P) \]
  \[ \lambda_{2\gamma}^0 = \frac{\lambda_S + 3\lambda_T}{4} = \lambda_A \approx 2 ns^{-1} \]

- Pore size < 1 nm -> \( \lambda_{3\gamma} \) neglected, only pick off annihilation

\[ \lambda_{TE} (R) = \lambda_A \left[ 1 - \frac{R}{R + \Delta R} \right] + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \]

- \( \Delta R = 0.166 \) nm determined by Eldrup and Jean
- Pore size > 1 nm -\( \lambda_{3\gamma} \) cannot be neglected, temperature dependence of o-Ps lifetime (excited states)

The TE model

- TE model valid for $r > 2\text{nm}$
- Very successful for open-volume characterization in polymers

Polymer research

PALS study of different polymers under CO$_2$ gas exposure and pressure densified (200 MPa)

The TE model (valid until 1 nm radius)

Fig. 5. The mean, $\langle \nu_h \rangle$, and the mean dispersion, $\sigma_h$, of the hole volume as a function of temperature $T$ for untreated (black), densified at 200 MPa (blue), and CO$_2$ gas-exposed and degassed (red) COC and PC.
Polymers under confinement conditions

### Polymers under confinement conditions

- 
  
## Table 1: Sample Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1 ) (ns)</th>
<th>( I_1 ) (%)</th>
<th>( \tau_2 ) (ns)</th>
<th>( I_2 ) (%)</th>
<th>( \tau_3 ) (ns)</th>
<th>( I_3 ) (%)</th>
<th>( \tau_4 ) (ns)</th>
<th>( I_4 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference PSiO(_2) empty</td>
<td>0.1194 ±0.0021</td>
<td>30.6 ±0.0047</td>
<td>27.28 ±0.66</td>
<td>1.652 ±0.0022</td>
<td>28.23 ±0.75</td>
<td>85.799 ±0.362</td>
<td>13.88 ±0.43</td>
<td></td>
</tr>
</tbody>
</table>

#### After filling the sample with polymer:

- Three component decomposition is very good (Variance = 1.13).

All component are free.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1 ) (ns)</th>
<th>( I_1 ) (%)</th>
<th>( \tau_2 ) (ns)</th>
<th>( I_2 ) (%)</th>
<th>( \tau_3 ) (ns)</th>
<th>( I_3 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPS in PSiO(_2)</td>
<td>0.1555 ±0.0016</td>
<td>35.8 ±0.0027</td>
<td>27.31 ±0.56</td>
<td>2.740 ±0.002</td>
<td>36.88 ±0.404</td>
<td></td>
</tr>
</tbody>
</table>

Wycliffe Kiprop Kipnusu
University of Leipzig,
Faculty of Physics and Earth Science
Institute of Experimental Physics I
Division of "Molecular Physics"
Linnestraße 5,
04103 Leipzig, Germany

- experiments planned to observe open volume in polymer under confinement
- shift of glass temperature?
- experiment just running…

≈10 nm diameter
Mesopores - Controlled pore glasses

IUPAC (International Union of Pure and Applied Chemistry)

- Micropores ( < 2 nm)
- Mesopores ( 2 - 50 nm)
- Macropores ( > 50 nm)
Controlled pore glasses - CPG

VYCOR-Process

alkali borosilicate glass

$T \rightarrow 530 - 710°C$

Extraction

$HCl/NaOH$

$d_p \ 1 \ to \ 110 \ nm$

- spinodal phase separation
- decomposition is initiated by heat treatment
- alkali rich borate phase $\leftrightarrow$ pure silica
- alkali phase soluable in acid $\rightarrow$ silica network
- pore size depends on basic material
- shape depends on duration and $T$ of heat treatment

Controlled pore glasses - CPG

porous microspheres:
- 100 µm

porous membranes:
- 20 x 20 x 0.2 mm

DE-Patent 19848377 A1
Model for $R > 1$ nm - RTE

- Rectangular TE model = RTE model (for 3D cubic pores):

\[
\lambda_{RTE}(D, T) = \lambda_A - \frac{\lambda_s - \lambda_{3\gamma}}{4} \left[ 1 - \frac{2\delta}{D} + \sum_{i=1}^{\infty} \frac{1}{i\pi} \sin \left( \frac{2i\pi\delta}{D} \right) e^{-\frac{\beta_i^2}{D^4kT}} \right] - \sum_{i=1}^{\infty} e^{-\frac{\beta_i^2}{D^4kT}}
\]

- Boltzmann statistics ascribes explicit temperature dependence to the lifetime

- Rectangular geometry -> prevention of complicated Bessel functions

- $\delta = 0.18$ nm analogous to TE model

---

The experiments at room temperature

- we measured porous glass in a broad pore size range
- pore size obtained by N$_2$-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size
The RTE model

Figure 5  (Top) Pore size calibration calculated at different temperatures versus mean-free path. (Bottom) Recent round-robin comparisons of PALS pore diameters with those measured by small-angle neutron scattering (SANS), ellipso-metric porosimetry (EP), and gas absorption (BET).
The T-dependence

- although we found good agreement for $T = 300$ K
- temperature behavior cannot be explained very well at low temperatures
- model too simple
Cryo-condensation of $N_2$ in CPG nano-pores

- S-parameter behaves similar like intensity of o-Ps lifetime component
- Cryo-condensation can be observed as filling of pores
- Phase transition can be studied in a nano-volume as function of size, gas, $T$, and $p$

$T = 80 \text{ K}$
$d = 16 \text{ nm}$

![Graph showing S-parameter vs. $p_{N_2}$ in mbar with adsorption and desorption curves.](image)
Loading of Mesopores by Drugs

- CPG membranes have been loading with Acetaminophen ($C_8H_9NO_2$) - also known as Paracetamol
- different pore sizes were studied
- filling by dropping membrane in hot melt of drug
- degree of filling can be studied with positrons
Loading of Mesopores by Drugs

- Filling almost complete for large pores (22 nm)
- Lifetime spectra show much smaller intensity for long-lived component
- Remaining pores are smaller

<table>
<thead>
<tr>
<th>Probe</th>
<th>Membrandicke</th>
<th>vor Bel.: $\tau_4$ und $I_4$</th>
<th>nach Bel.: $\tau_4$ und $I_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22 nm</td>
<td>300 $\mu$m</td>
<td>121 ns 6,2 %</td>
<td>111 ns 0,5 %</td>
</tr>
<tr>
<td>9,3 nm</td>
<td>300 $\mu$m</td>
<td>98 ns 7,8 %</td>
<td>58 ns 0,9 %</td>
</tr>
<tr>
<td>3 nm</td>
<td>500 $\mu$m</td>
<td>47 ns 11,7 %</td>
<td>52 ns 5,0 %</td>
</tr>
<tr>
<td>2,2 nm</td>
<td>300 $\mu$m</td>
<td>30,7 ns 14,3 %</td>
<td>19,7 ns 4,0 %</td>
</tr>
</tbody>
</table>
Loading of Mesopores by Drugs

- pdf = probability density function
- Example: membrane with 2.2 nm pore
- distribution of pore sizes is shifted to smaller values
- 30.7 ns corresponds to 2.2 nm and 19.7 ns -> 1.5 nm
Small pores in the wall of larger pores

Transformation of porous glasses into MCM-41 containing geometric bodies

Hans Uhlig a,*, Marie-Luise Gimpel a, Alexandra Inayat b, Roger Gläser a, Wilhelm Schwieger b, Wolf-Dietrich Einicke a, Dirk Enke a

a University of Leipzig, Institute of Chemical Technology, Linnéstr. 2, 04109 Leipzig, Germany
b University of Erlangen-Nuremberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of tenside solution in ml</th>
<th>new sample name</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA-01</td>
<td>40</td>
<td>MCM-40</td>
</tr>
<tr>
<td>GA-02</td>
<td>35</td>
<td>MCM-35</td>
</tr>
<tr>
<td>GA-03</td>
<td>30</td>
<td>MCM-30</td>
</tr>
<tr>
<td>GA-04</td>
<td>42</td>
<td>MCM-42</td>
</tr>
<tr>
<td>GA-05</td>
<td>25</td>
<td>MCM-25</td>
</tr>
<tr>
<td>GA-06</td>
<td>20</td>
<td>MCM-20</td>
</tr>
<tr>
<td>GA-14</td>
<td>10</td>
<td>MCM-10</td>
</tr>
<tr>
<td>GA-15</td>
<td>5</td>
<td>MCM-05</td>
</tr>
</tbody>
</table>

LN2 adsorption
Small pores in the wall of larger pores

- solvent (MCM) was added into a larger pore system
- large pores: 15 nm
- small pores are formed in the walls: 4 nm

Conventional data analysis
amount of solvent

data analysis by MELT

4 nm pores

15 nm pores

intensity (%)
lifetime (ns)
The Slow-Positron Beam Technique

- broad positron emission spectrum from beta sources
- deep implantation into solids
- no use for study of defects in thin layers
- moderation necessary

Mean implantation depth of un-moderated positrons (1/e): Si: 50µm
Moderation of Positrons

W (110) single crystal foil (negative workfunction)

2 μm

fraction

annihilation ≈ 13%

monoenergetic positrons ≈ 0.05%

E ≈ 3 eV

fast positrons ≈ 87%

up to several 100 keV

moderation efficiency: ≈ 10^{-4}
Low-K dielectric layers

- modern ultra-large scale microprocessors suffers from long relaxation times
- information transport is limited by product $R \times C$
- $R$ has been decreased: Copper technology (instead of Al)
- $C$ is relatively high when $SiO_2$ is used as isolation layer; $\varepsilon_r=4$

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

- low-k (small $\varepsilon_r = 2...2.5$) layers may help
- these are layers with micropores with pore size of $d \approx 1$ nm with high porosity
- problem for characterization: closed porosity

![Diagram of Low-K dielectric layers](image)
Low-K dielectric layers

Delay as Function of Feature Size

- Interconnect delay with Cu and low-k
- Interconnect delay with Al and SiO2
- Sum of Gate, Cu and low-k delays
- Sum of Gate, Al and SiO2 delays
- Gate delay

Delay (ps)

Generation (microns)
**Low-K dielectric layers**

- Positrons are ideal tool for closed porosity in low-k layers
- Lifetime spectra of differently treated low-K layers
- Treatment:
  - untreated porous layer
  - plasma treatment for compaction
  - TiN cap layer
Low-K dielectric layers

- dispersion of lifetime gives the size distribution of the pore system
Low-K dielectric layers

- Monoenergetic positrons can be used to depth scan the layer.
- Monoenergetic positrons are obtained by moderation.

Graph showing the mean penetration depth and pore size as functions of positron energy.
Summary

- for T = 300 K general agreement to the RTE model -> at room temperature
- PALS is a useful porosimetry tool

- Advantages:
  - very sensitive method for small pores (0.3 to 10 nm)
  - upper sensitive limit \( \approx \) 60 nm
  - non-destructive method
  - also for closed pore systems
  - applicable also for thin layers (50 ... 2000 nm)
“A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it.”

Albert Einstein (American German 1879-1955)