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# Kinetic Study on the Doping Level of ABPBI Membrane

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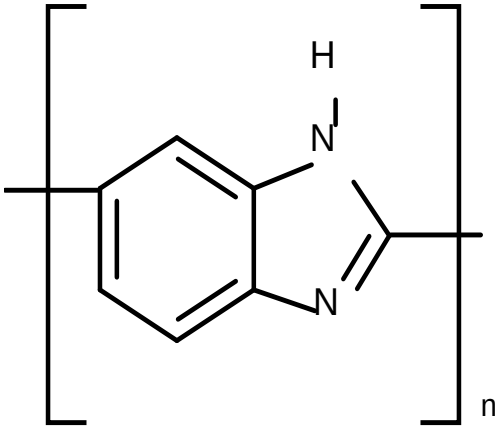
Institute of Energy and Climate Research IEK-3: Electrochemical Process Engineering

# Outline

- ABPBI membrane
- Doping process
- Doping level
- Rate law
- Activation energy

# ABPBI membrane

ABPBI: poly(2,5-benzimidazole)



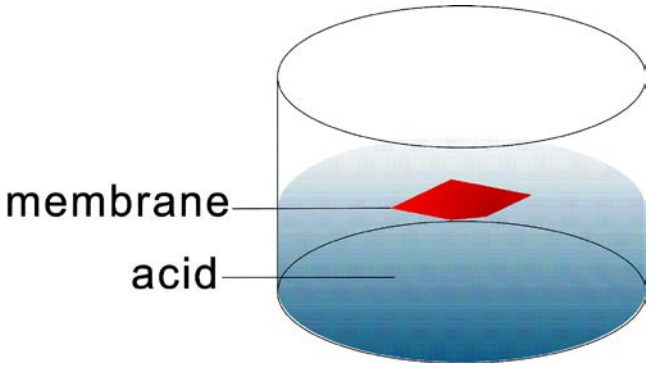

Current membrane: cross-linked ABPBI polymer

exact structure Fuma-Tech (Germany) confidential

# Doping process

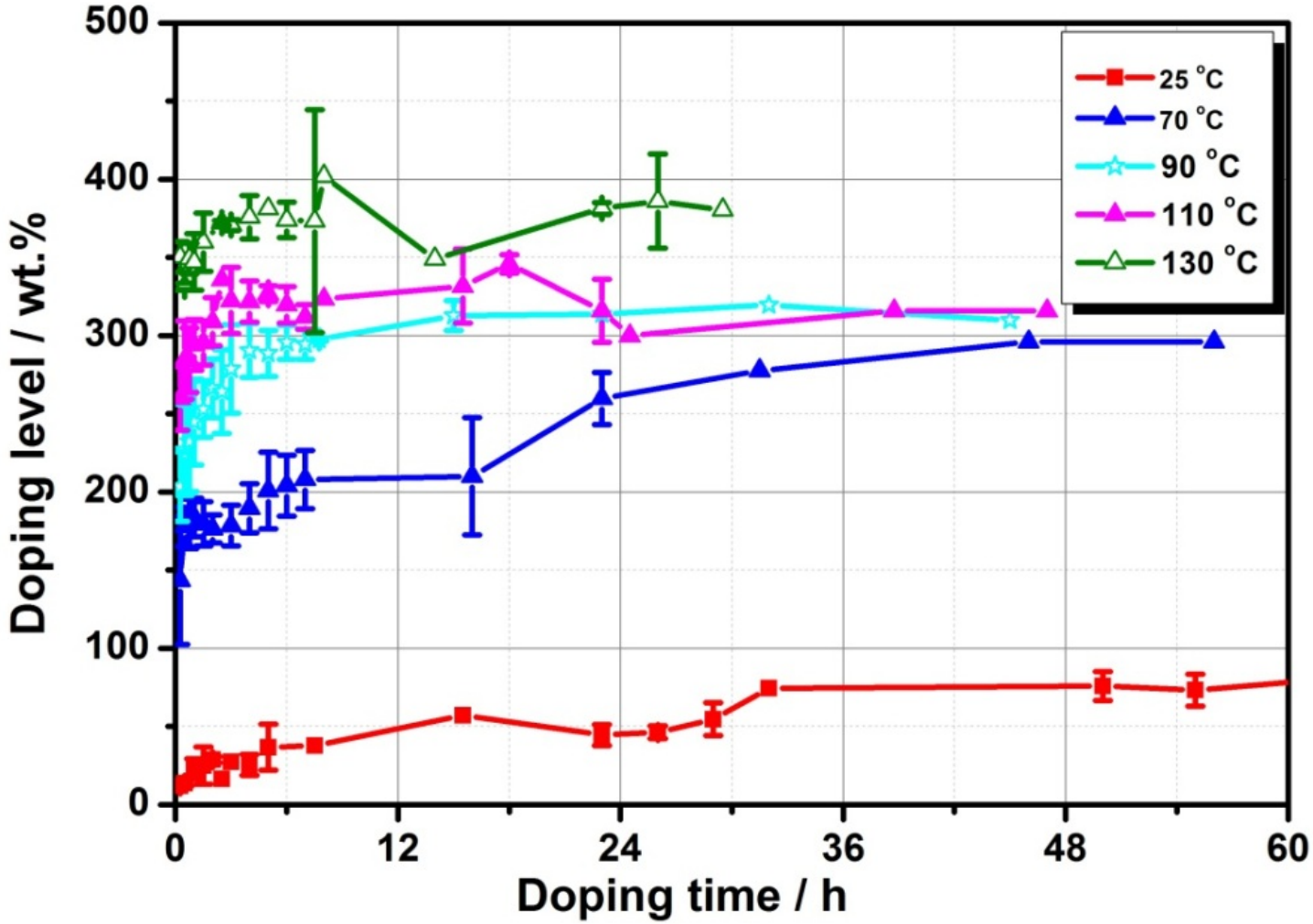
- Membrane is heated in an open acid bath
- Acid: 85 wt.% phosphoric acid
- Drying surface with tissues

$$\text{acid doping level} = \frac{W_a}{W_m} \times 100\,\%$$




- $W_m$ / g: weight of membrane
- $W_a$ / g: weight of acid in doped membrane

# Doping level

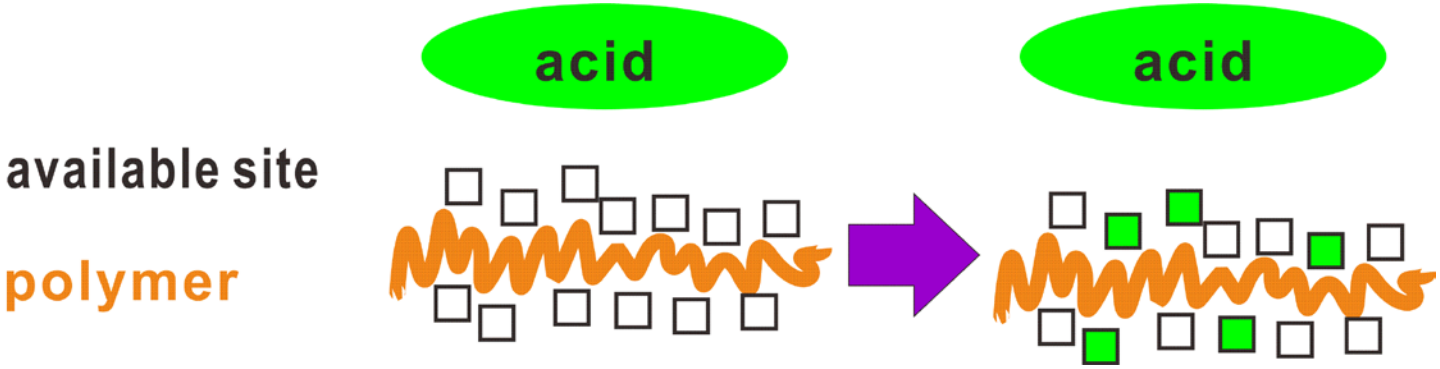



- Higher doping temperature ⇨ faster to equilibrium, higher doping level
- At 130 °C, membrane dissolved more and more after 12 h.

# Available sites for adsorption

Assumptions for doping membrane:

- The doping process: an adsorption process.
- The real reaction between acid and polymer: not regarded.
- Each acid molecule: at a specific volume close to the polymer chain.
- The specific volume: available site, L.




$$L + acid \leftrightarrow L \cdot acid$$

- Reaction: acid & available sites
- Amount of available sites: single digit for each polymer repeat unit
  constant at a certain temperature

# Occupied site fraction

Supposing membrane contains *n* repeat unit

$$\text{Doping level} = \frac{\text{acid weight}}{\text{membrane weight}} \times 100\% = \frac{x \cdot A}{n \cdot M} \times 100\%$$

$$\text{Amount of total available site} = n \cdot l$$

$$\mathrm{L} + \mathrm{acid} \leftrightarrow \mathrm{L} \cdot \mathrm{acid}$$

$$\text{Amount of occupied sites} = \text{amount of adsorbed acid} = x$$

$$\text{Occupied site fraction} = \frac{x}{n \cdot l} = \text{doping level} \times \frac{M}{l \cdot A \cdot 100\%}$$

- Occupied site fraction ~ doping level.

| | |
|---|---|
| $x$ / mol: | amount of acid in doped membrane; and amount of occupied sites |
| $n$ / mol: | amount of polymer repeat unit |
| $l$ / mol mol$^{-1}$: | amount of available sites per polymer repeat unit |
| $A$ / g mol$^{-1}$: | molar mass of acid |
| $M$ / g mol$^{-1}$: | molar mass of polymer repeat unit |

# Adsorption rate

Total sites
$[L]_T$= max. acid doping level

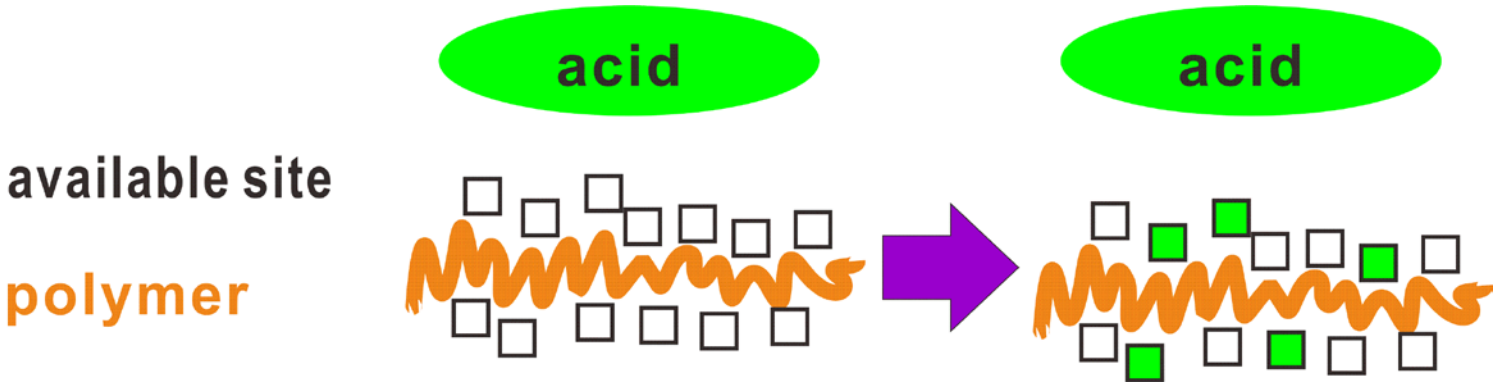
Occupied sites
$[L]_B$= acid doping level

$$L + \text{acid} \leftrightarrow L \cdot \text{acid}$$

| | | | |
|---|---|---|---|
| $t = 0$ | $[L]_T$ | $C_0$ | 0 |
| $t = t$ | $[L]_F$ | $C_1$ | $[L]_B$ |
| $t = t_e$ | $[L]_F$ | $C_2$ | $[L]_e$ |

Free sites
$[L]_F = [L]_T - [L]_B$

If $C_0$ high enough, $[L]_e \approx [L]_T$



# Reaction rate law

- Pseudo-first-order reaction rate law
- Pseudo-second-order reaction rate law

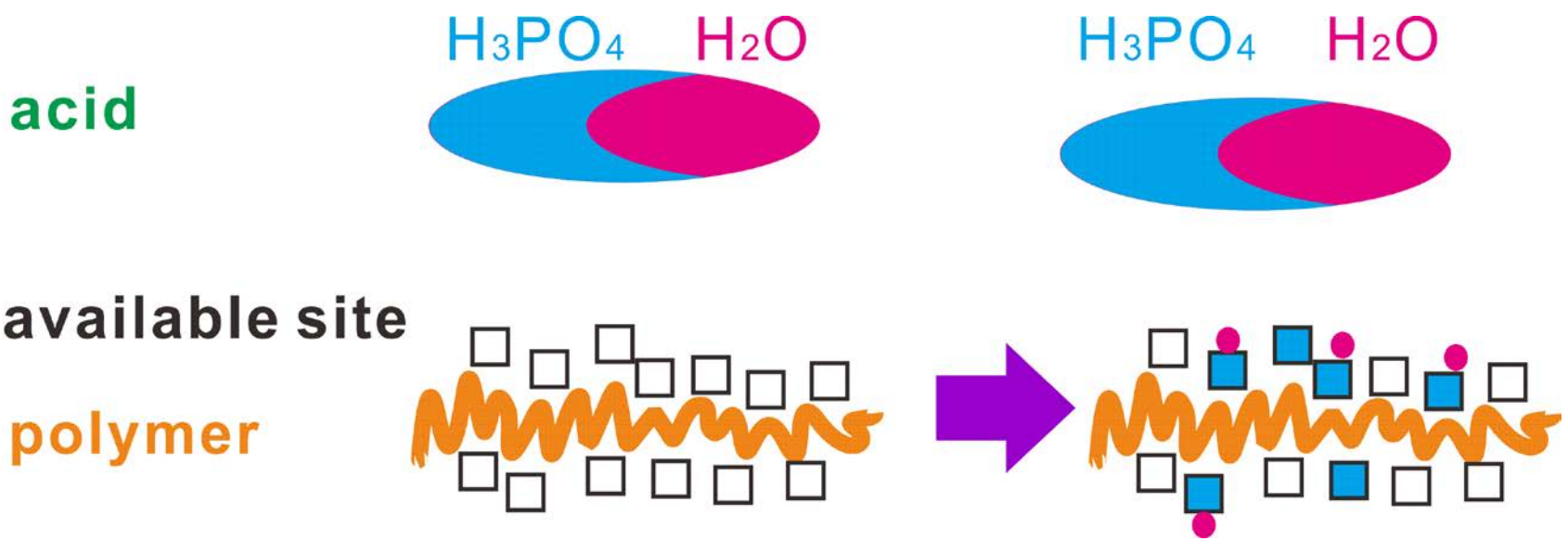
Y.S. Ho, Process Biochemistry 34 (1999) 451-465

# Pseudo-first-order reaction rate law

Assumptions:

- Acid concentration in the acid bath does not change during doping process.
- Occupation of $H_2O$ on the available sites is negligible.

$$L + H_3PO_4 + xH_2O \leftrightarrow L \cdot (H_3PO_4 \cdot xH_2O)$$



# Pseudo-first-order reaction rate law

$$L + H_3PO_4 + xH_2O \leftrightarrow L \cdot (H_3PO_4 \_ xH_2O)$$

| | | | | |
|---|---|---|---|---|
| $t = 0$ | $[L]_T$ | $C_0$ | $C_0'$ | 0 |
| $t = t$ | $[L]_T - [L]_B$ | $C_0$ | $C_0'$ | $[L]_B$ |

$$r = -\frac{d([L]_T - [L]_B)}{dt} = k_1 C_0 C_0' ([L]_T - [L]_B) = k_1' ([L]_T - [L]_B)$$

$$\log([L]_T - [L]_B) = \log[L]_T - \frac{k_1'}{2.303} t \quad \Rightarrow \quad \log([L]_T - [L]_B) \sim t$$

Real doping level

Equilibrium doping level

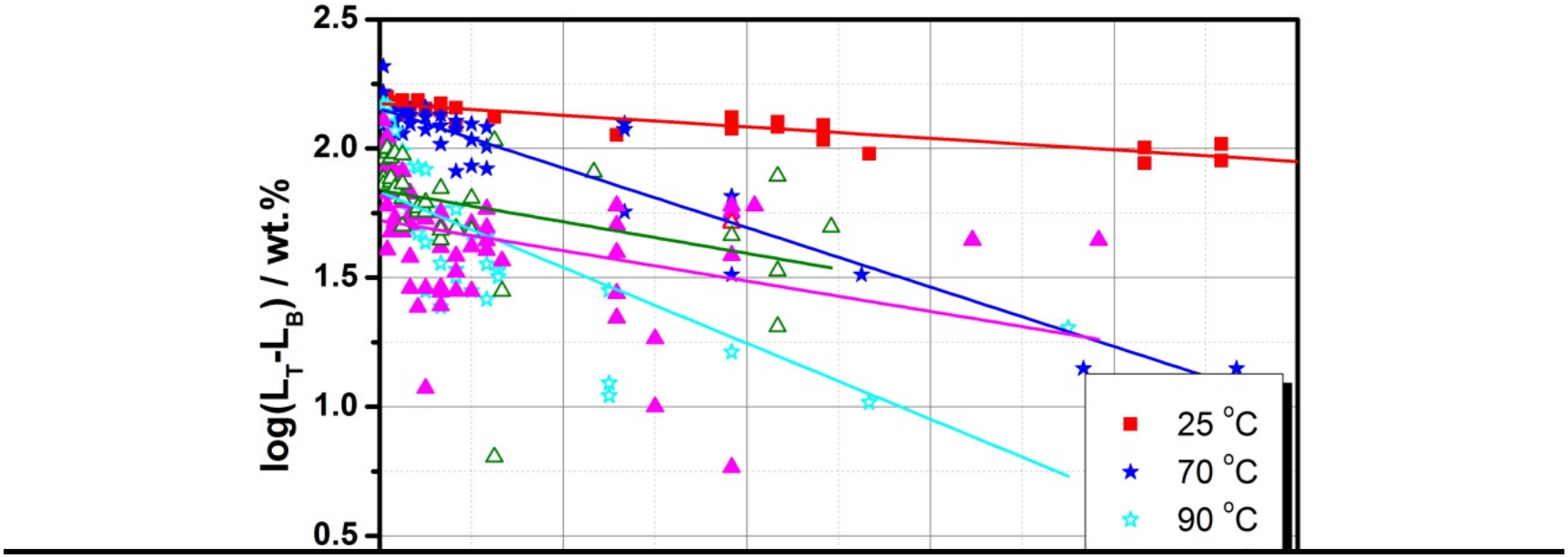
$C_0$ □ $C_0'$ : original $H_3PO_4$ and $H_2O$ concentration

r : reaction rate

$k_1$ : true reaction rate constant

$k_1'$ : Pseudo - first - order rate constant

# Pseudo-first-order reaction rate law



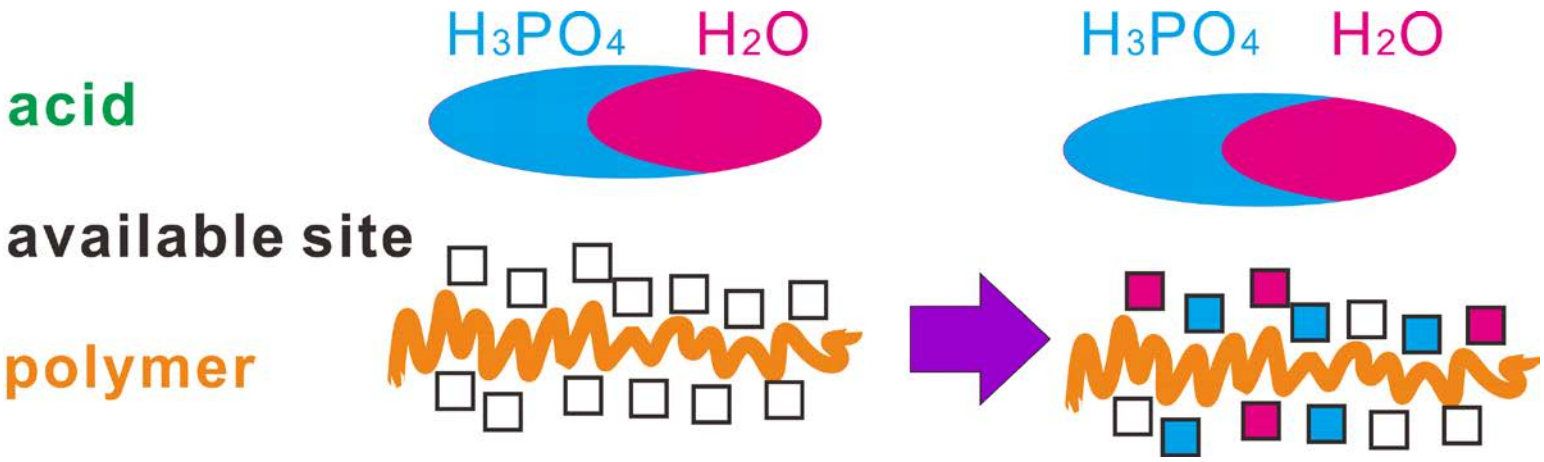

| Doping temperature / °C | Experimental equilibrium doping level / wt.% | Calculated equilibrium doping level / wt.% | $R^2$ |
|---|---|---|---|
| 25 | 163 | 143.1 | 0.95399 |
| 70 | 296 | 130.1 | 0.72469 |
| 90 | 320 | 56.0 | 0.42258 |
| 110 | 354 | 49.3 | 0.10872 |
| 130 | 349 | 22.7 | -0.04758 |

- Pseudo-first-order model: only for doping at room temperature.

# Pseudo-second-order reaction rate law

- Assumption:
- Acid concentration in the acid bath remains stable during doping process.
- Both H3PO4 and H2O are able to occupy available sites.

$$2L + H_3PO_4 + H_2O \leftrightarrow L \cdot H_3PO_4 + L \cdot H_2O$$



# Pseudo-second-order reaction rate law

$$2L + H_3PO_4 + H_2O \leftrightarrow L \cdot H_3PO_4 + L \cdot H_2O$$

| | | | | | |
|---|---|---|---|---|---|
| $t = 0$ | $[L]_T$ | $C_0$ | $C_0'$ | 0 | 0 |
| $t = t$ | $[L]_T - [L]_B$ | $C_0$ | $C_0'$ | $[L]_{H_3PO_4}$ | $[L]_{H_2O}$ |

$$[L]_B = [L]_{H_3PO_4} + [L]_{H_2O}$$

$C_0, C_0'$ : concentration of $H_3PO_4$ and $H_2O$ in acid

$k_2'$ : Pseudo-second-order rate constant

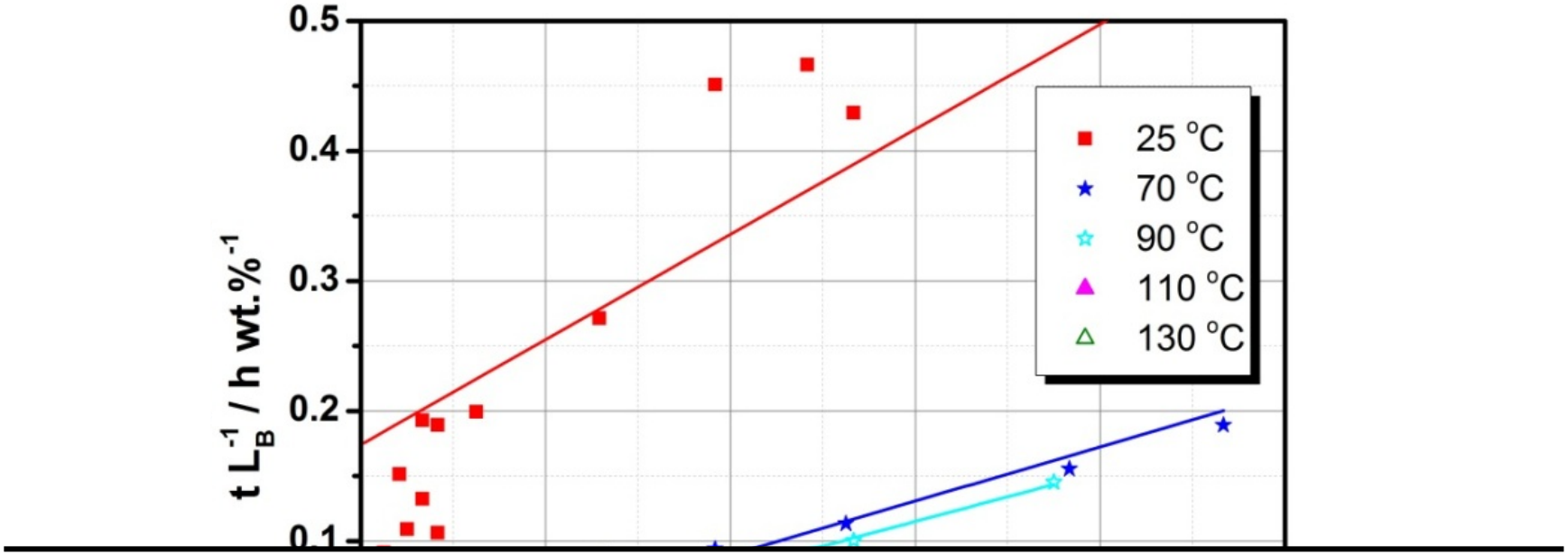
$$r = -\frac{d([L]_T - [L]_B)}{dt} = k_2'([L]_T - [L]_B)^2$$

$$\frac{t}{[L]_B} = \frac{1}{k_2'[L]_T^{\,2}} + \frac{1}{[L]_T}t \quad \rightarrow \quad \frac{t}{[L]_B} \sim t$$

Real doping level

Equilibrium doping level

# Pseudo-second-order reaction rate law




| Doping temperature / °C | Experimental equilibrium doping level / wt.% | Calculated equilibrium doping level / wt.% | $R^2$ |
|---|---|---|---|
| 25 | 163 | 148.3 | 0.83283 |
| 70 | 296 | 288.4 | 0.97529 |
| 90 | 320 | 315.9 | 0.99906 |
| 110 | 354 | 323.4 | 0.99313 |
| 130 | 349 | 382.6 | 0.99518 |

- The Pseudo-second-order model: for doping process from 70 to 130 °C

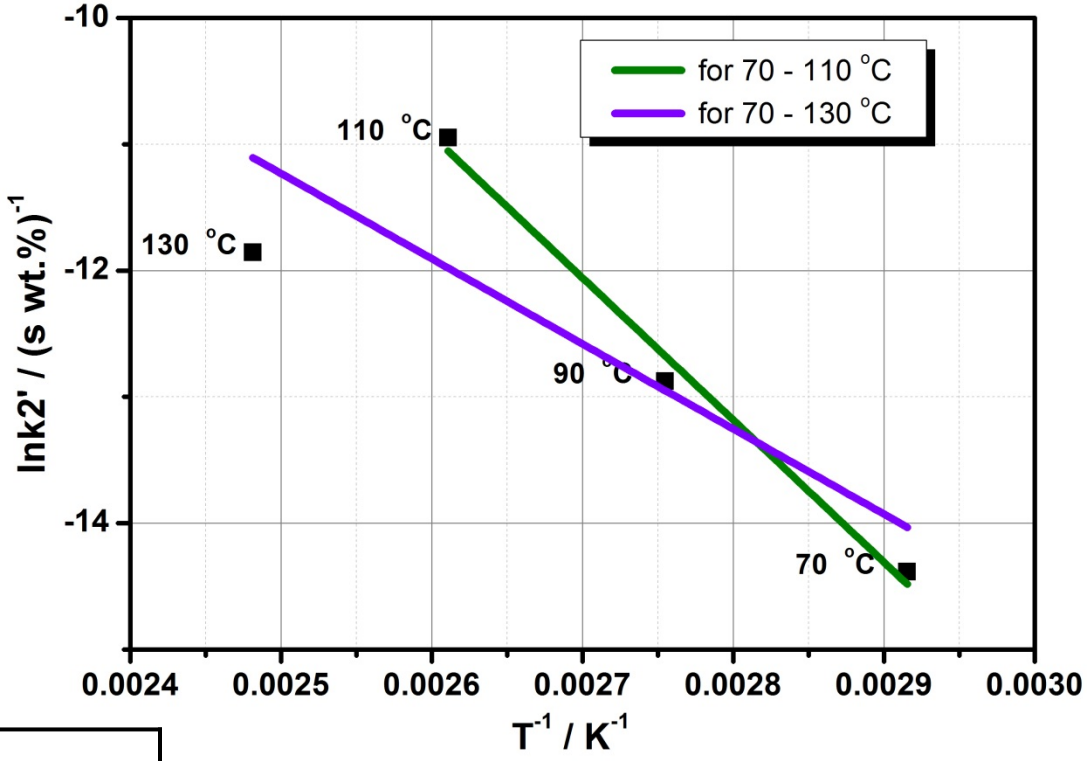
# Arrhenius Equation

Based on pseudo-second-order reaction rate law

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

$$k_2' = k_2 C_0 C_0'$$

$$ln k_2' = c - \frac{E_a}{R}\frac{1}{T}$$




| | |
|---|---|
| *Ea* / kJ mol$^{-1}$: | Activation energy |
| *R* / J (mol K)$^{-1}$: | Gas constant, 8.314 |
| *T* / K: | Temperature |
| *c*: | constant related to the acid concentration |

For 70 - 110 °C: $Ea \approx 90\ \mathrm{kJ\ mol^{-1}}$

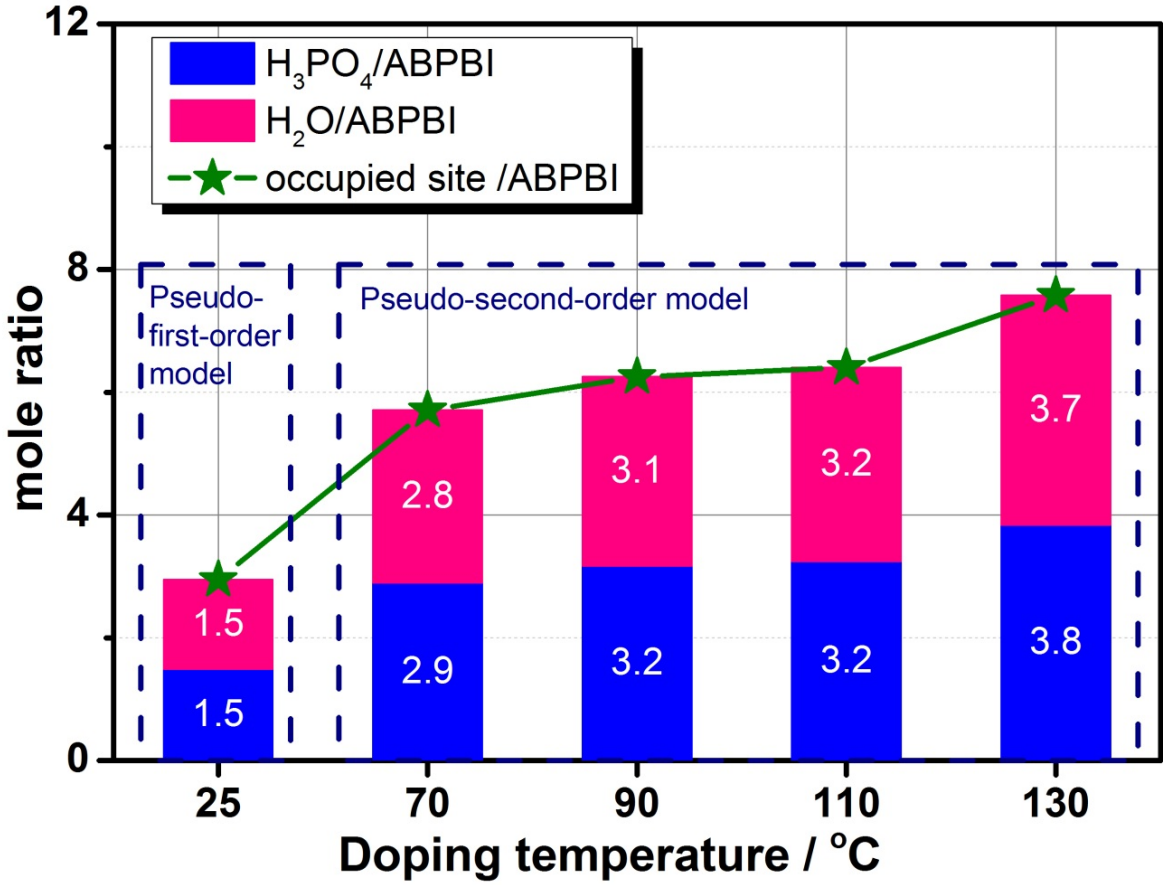
For 70 - 130 °C: $Ea \approx 60\ \mathrm{kJ\ mol^{-1}}$

# Amount of available sites

In 85 wt.% H3PO4 solution, $[H_3PO_4]/[H_2O] \approx 1$

Supposing: $[H_3PO_4]/[H_2O]$ in the acid bath keeps stable during the doping process.

$[H_3PO_4]/[H_2O]$ in the doped membrane keeps the same as acid bath.




* At 130 °C, the membrane was dissolved in a short time. The value is not reliable completely.

# Conclusion

- The rate law of doping process:

  at room temperature: fitted with the pseudo-first-order reaction rate law;

  at 70 ~ 130 $^{o}$C: fitted with the pseudo-second-order reaction rate law.

- The activation energy of doping from 70 to 130 $^{o}$C is about 90 kJ mol$^{-1}$.

# Thank you for your attention!