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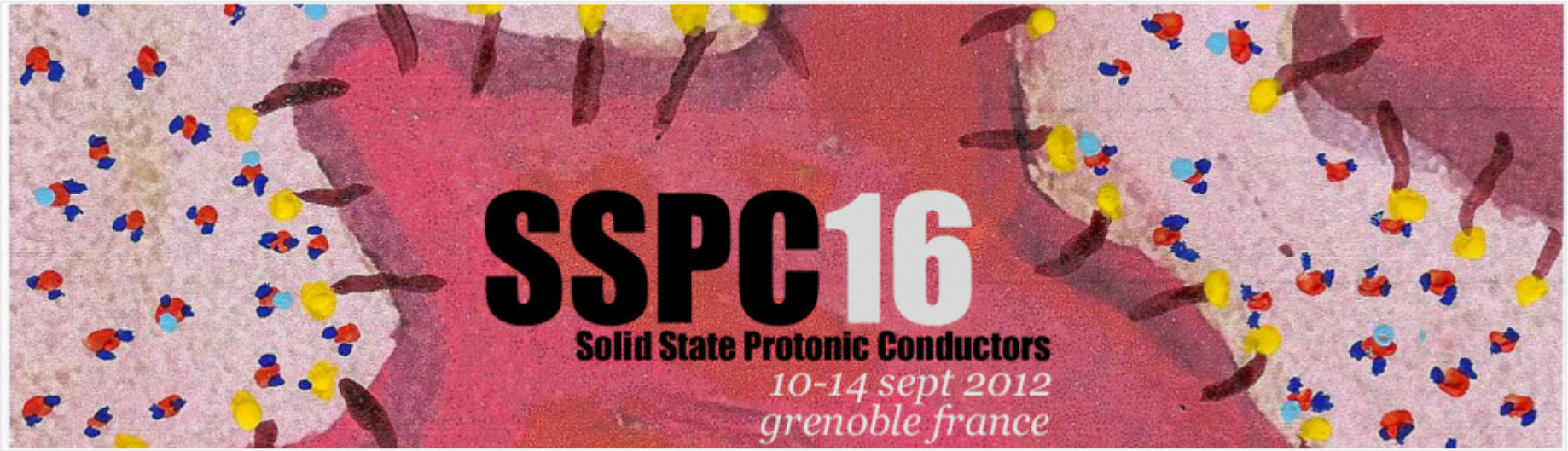


Proton Conductivity of Refractory Metal Phosphates at Intermediate Temperatures

Qingfeng Li, Yunjie Huang, Tatiana Anfimova,
Jens Oluf Jensen, Erik Christensen and Niels. J. Bjerrum

Section of Proton Conductors
Department of Energy Conversion and Storage
Technical University of Denmark, Kemitorvet 207, DK-2800 Lyngby, Denmark
Email: qfli@dtu.dk

Outlines

Introduction

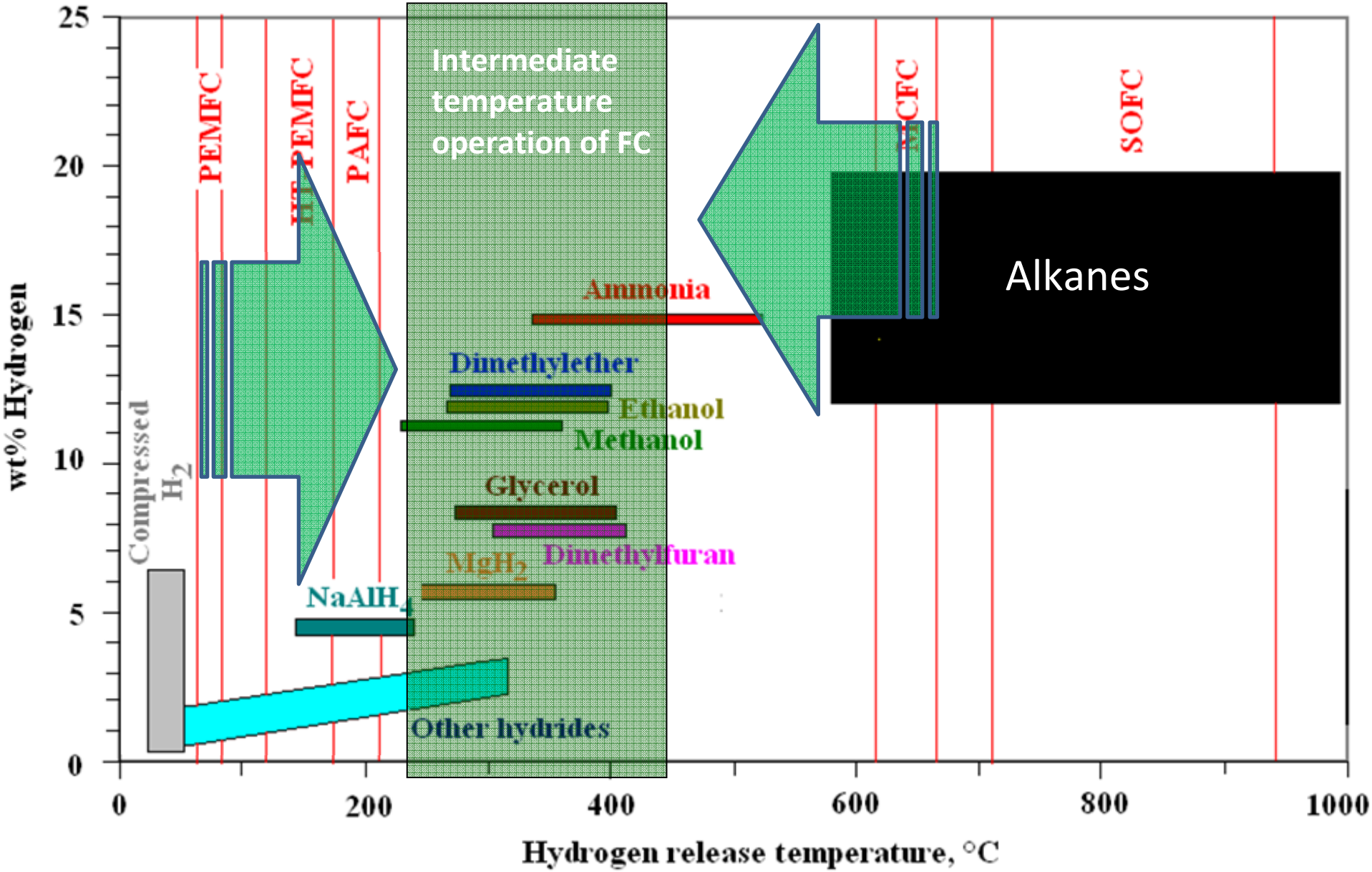
- Refractory metals and their phosphates

Niobium phosphates

- Anhydrous Conductivity
- Heat Treatment Temperature
- Crystalline forms
- Indium doping
- Morphology effects – sol-gel method
- Further stability evaluation
- OCV & EMF

Conclusions

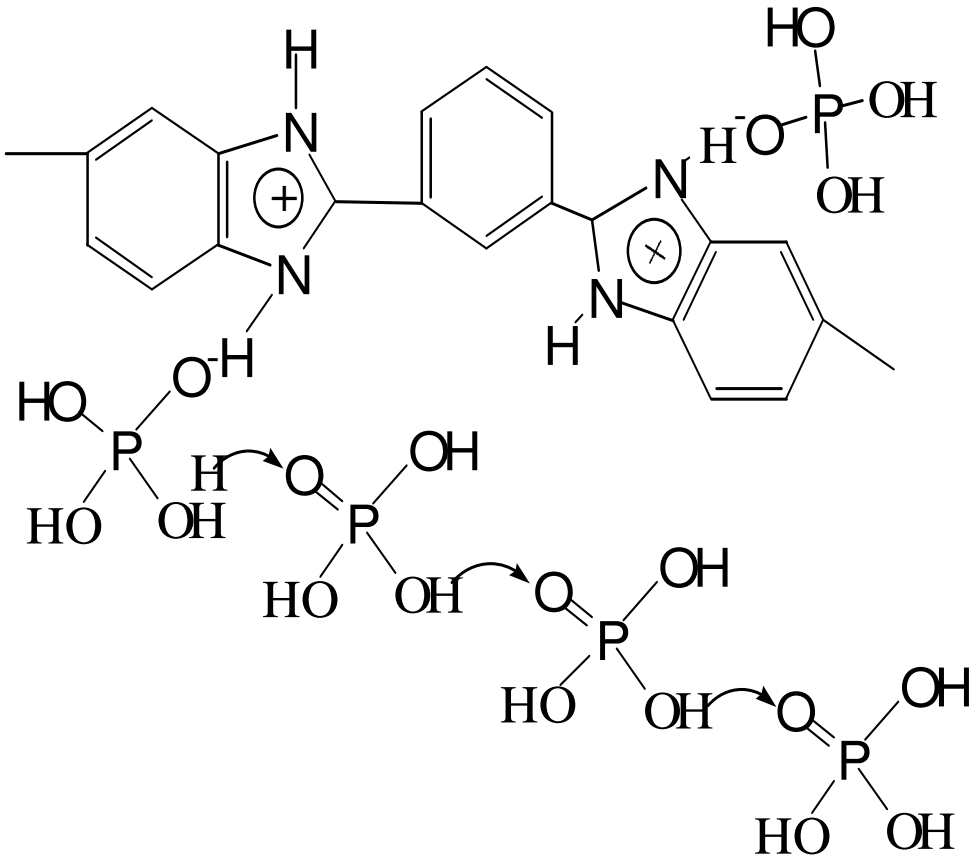
Intermediate temperature operation
- and fuelling of fuel cells



PBI/PA Conductivity

H_3PO_4 Protonates PBI

- **IR measurements indicate max protonation at n=2**
- Very low conductivity with n<2 indicating little N-H to N-H proton hopping
- **$H_2PO_4^-$ predominates over concentration range (n=6)**
- Low activation volume measured
- **t_{H+} measured ~.98 for n=6**
- Activation energy consistent with Grotthuss mechanism



Above 200°C

- **Acid condensation**
- **Acid evaporation**
- **Polymer degradation**
- **……**

Refractory metal oxides

Vanadium, Niobium, Tantalum……

- High surface acidity
  - Lewis acid sites Me=O
  - Brønsted acid sites Me-OH
- Solid acid catalysts for reactions such as
  - esterification
  - polycondensation
  - dehydration

÷ Significantly decreased acidity at elevated temperatures (below 700 K)

Refractory metal phosphates

- Phosphoric acid treated oxides
- Further increased surface acidity
  - both Me-OH and P-OH
- Acidity preserved at elevated temperatures
  - due to formation of polyphosphates

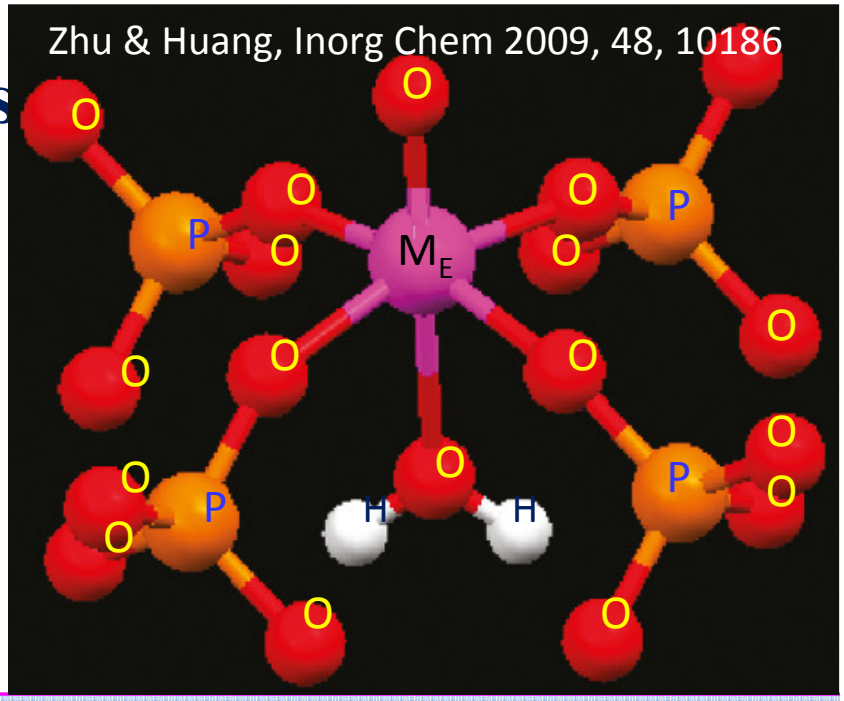
Vanadium & niobium phosphates

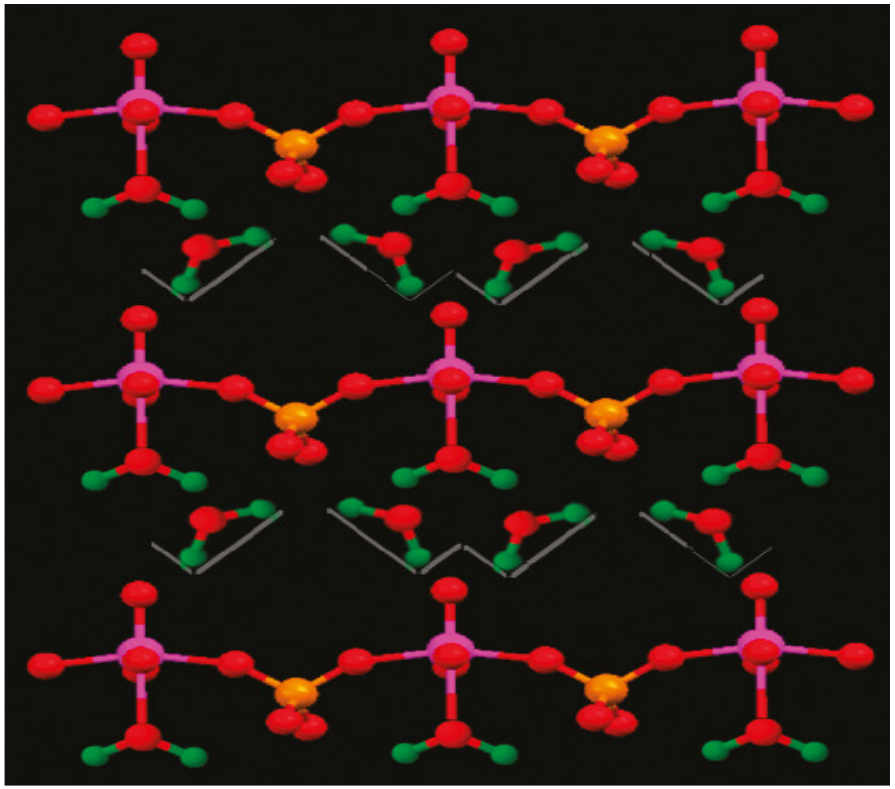
Layered structure

$VPO_5 \cdot H_2O$ or $VOPO_4 \cdot H_2O$

$NbPO_5 \cdot H_2O$ or $NbOPO_4 \cdot H_2O$

M_EO_6 octahedra
connected to four PO_4 tetrahedra
one axial group M_E=O
other axial ligands (H_2O)





- With both Lewis and Brønsted acid sites
  - strong acidity and catalytic activities towards acid-catalyzed reactions
- Layered/3-dimension structures
  - intercalation capacity of the interlamellar space
    - ammonia, amines, alcohols
    - acid molecules H_3PO_4, H_2SO_4, etc
  - strong hydrogen bonding involved

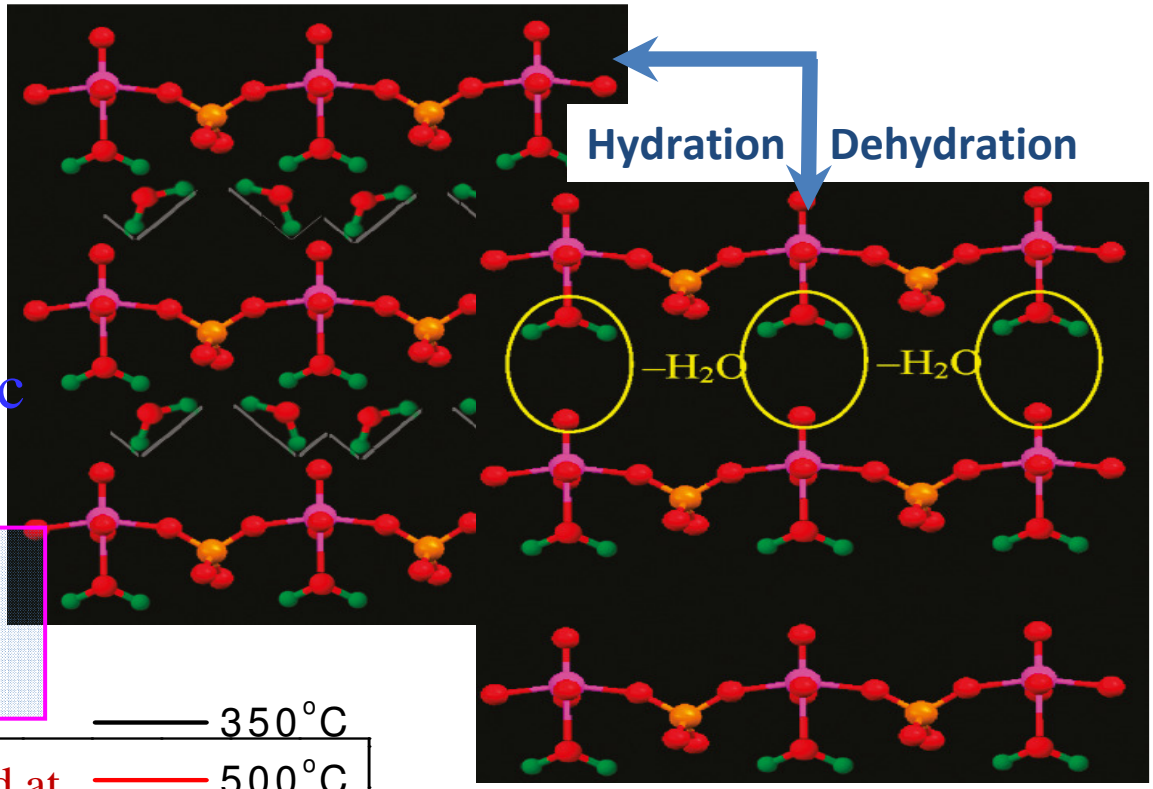
Nb phosphates

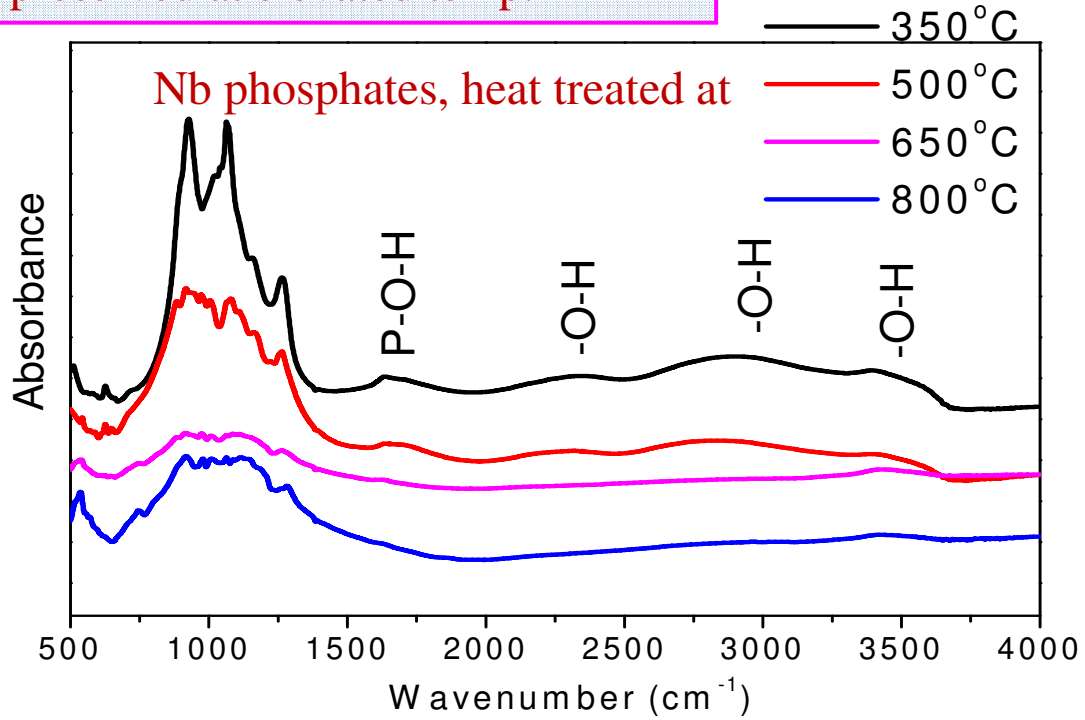
and Vanadium phosphates

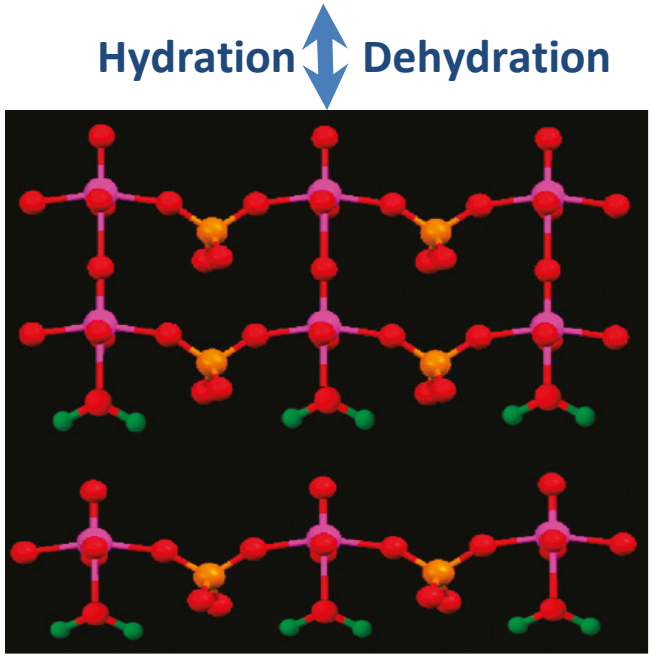
- up to 5 H_2O molecules
- dehydration at HT
  led to P-O-P/Nb-O-P bonds
- reversible hydr./dehydr.

Both Nb-OH and P-OH

preserved at elevated temp.





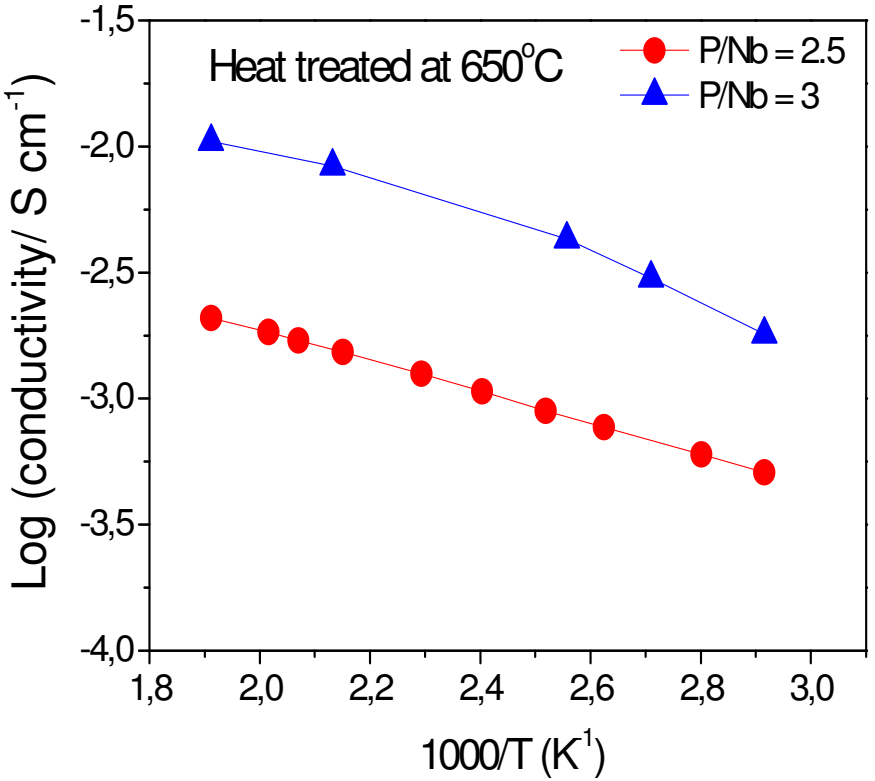


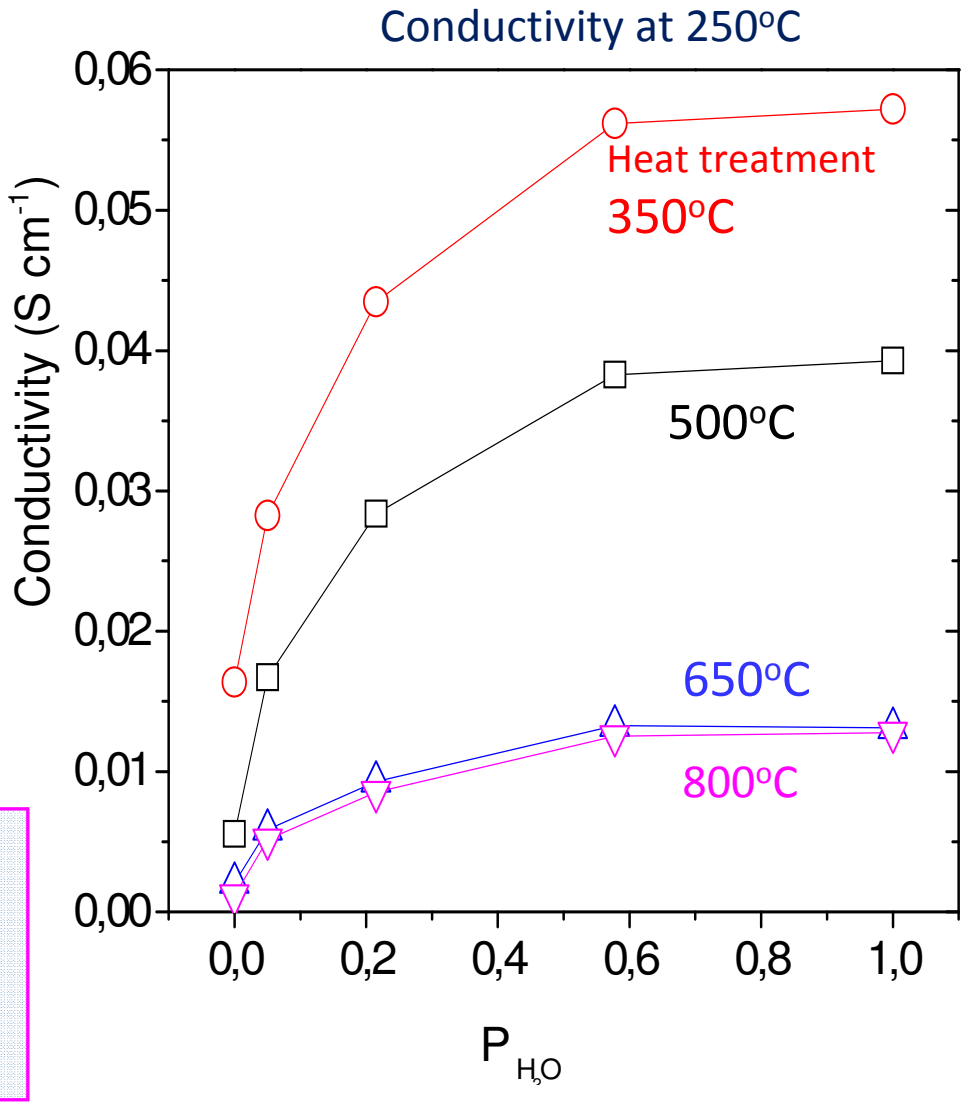
Anhydrous Conductivity

and water vapor dependence

Strong dependence

- on heat treatment temperature
- on atmospheric humudity





Anhydrous conductivity

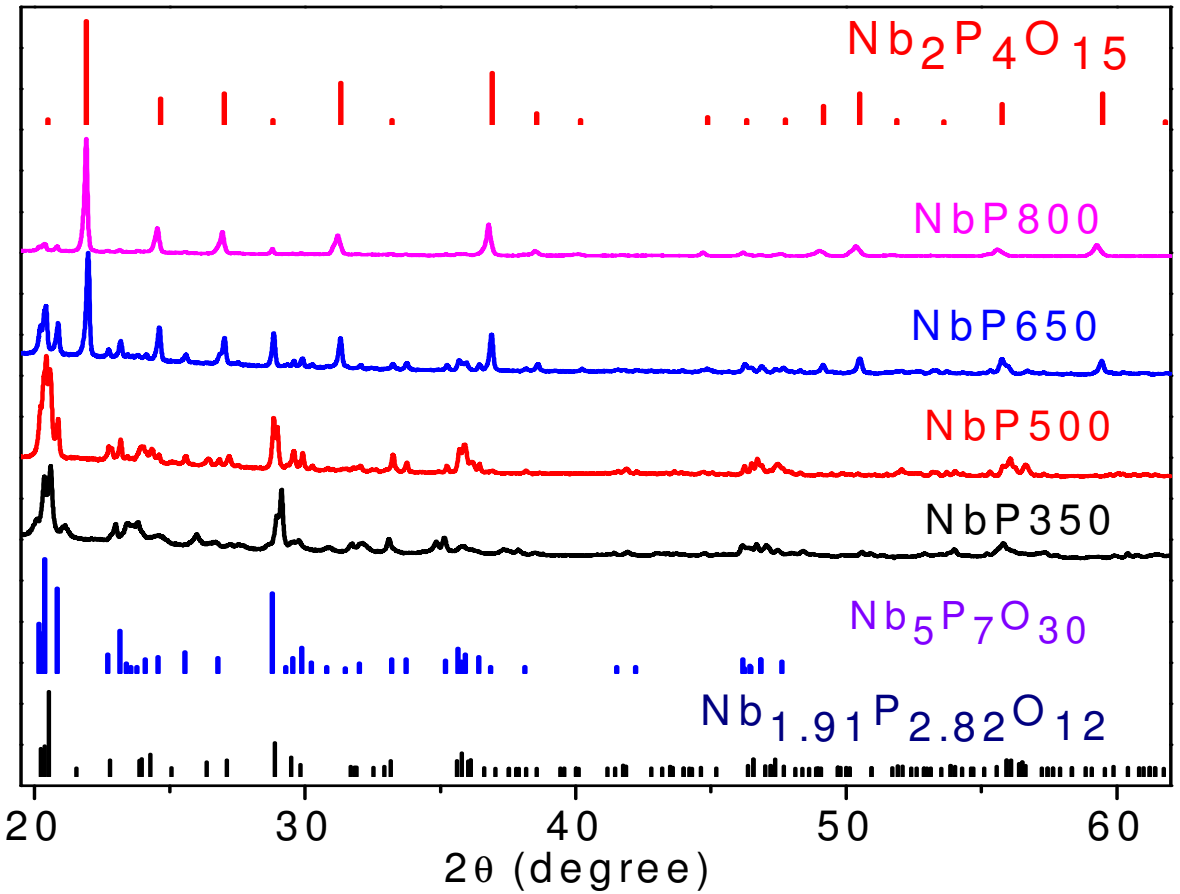
with an activation energy of 16-24 kJ mol^{-1}

- typical for the Grotthuss mechanism of proton migration in condensed phases

Heat Treatment Temperature

- phosphate structures

P/Nb = 2.0



Synthesis	
Initial molar ratio P/Nb	Heat treatment temperature (°C)
P/Nb = 4.0	*650*
P/Nb = 3.0	350 500 *650* 800
P/Nb = 2.5	350 500 650 800
P/Nb = 2.0	350 500 650 800

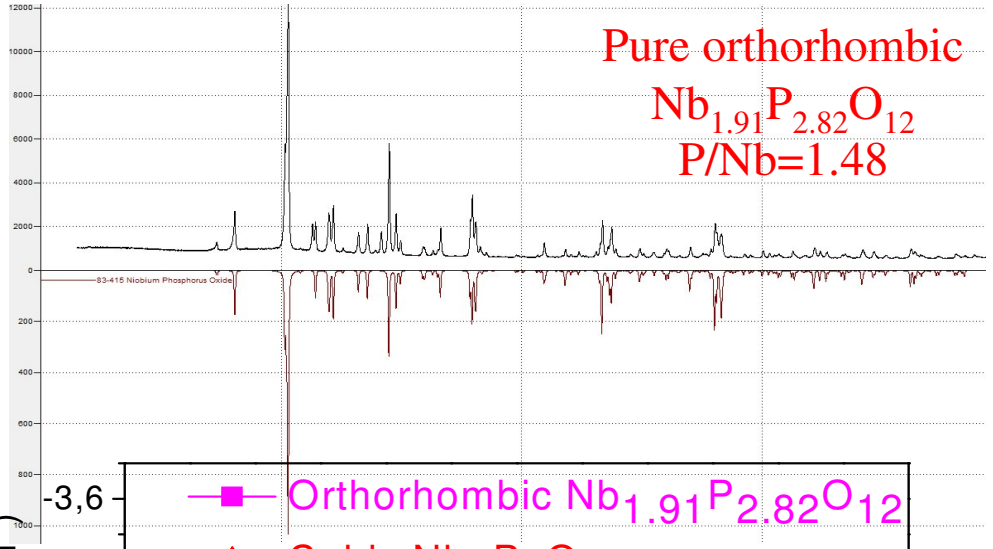
	Theoretic. density, g/cm^3	Crystal parameters of unit cell						Notes
		a	b	c	α	β	γ	
Monoclinic $Nb_5P_7O_{30}$	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT
Cubic $Nb_2P_4O_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT
Orthorhombic $Nb_{1,91}P_{2,82}O_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase Favors at LT

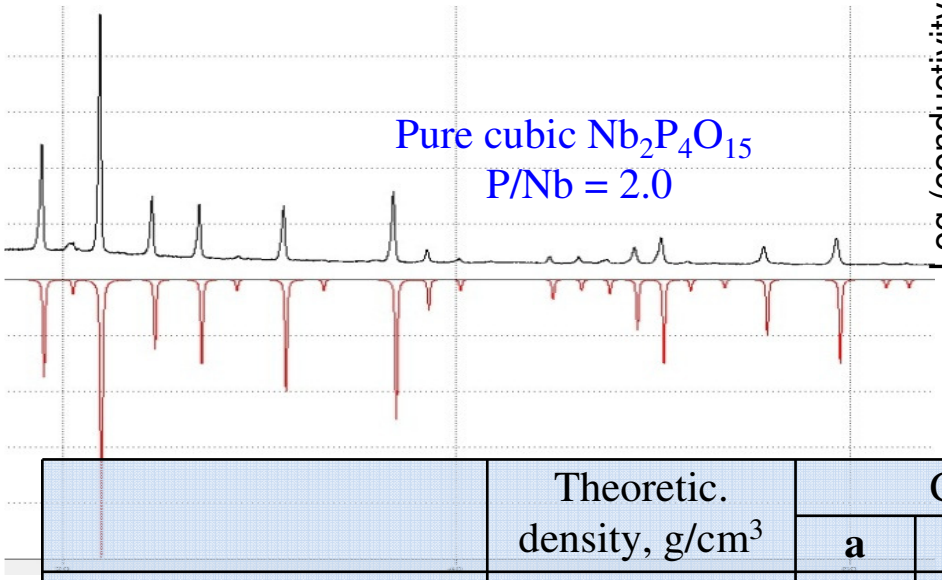
Crystalline forms

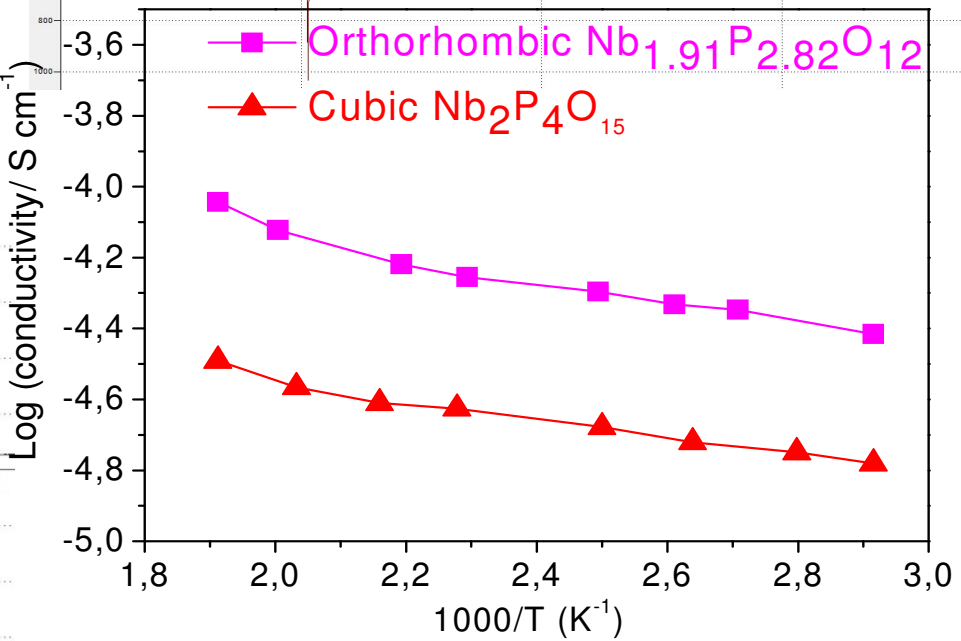
- Orthorhombic $Nb_{1.91}P_{2.82}O_{12}$
- Cubic $Nb_2P_4O_{15}$

Anhydrous conductivity

- **Orthorhombic $Nb_{1.91}P_{2.82}O_{12}$**
  - higher anhydrous conductivity in the whole temperature range







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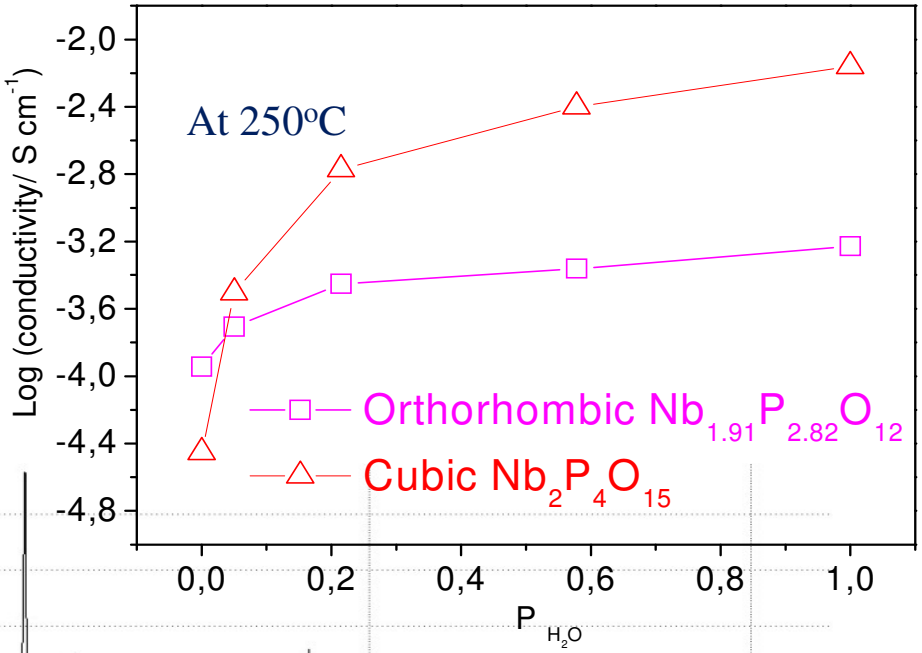
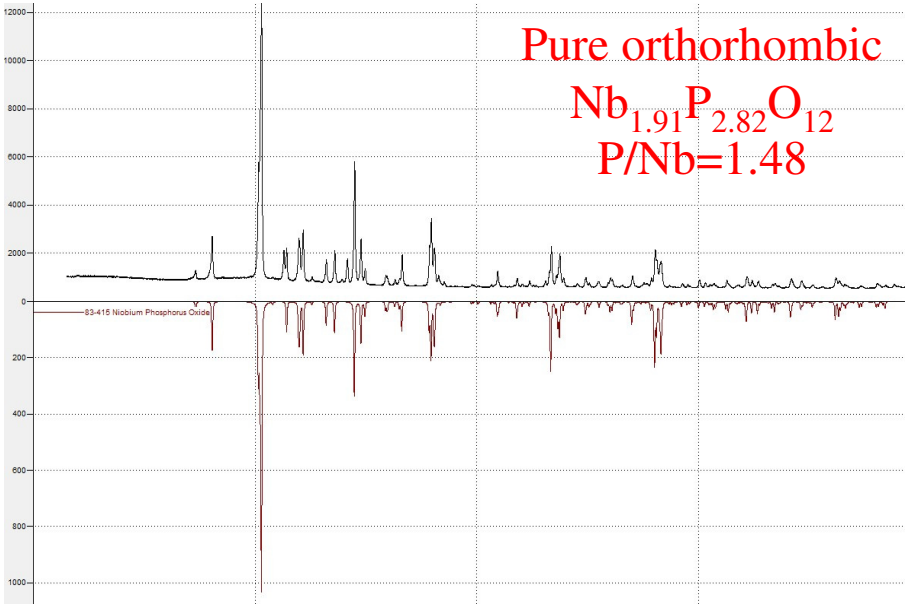
Crystalline forms

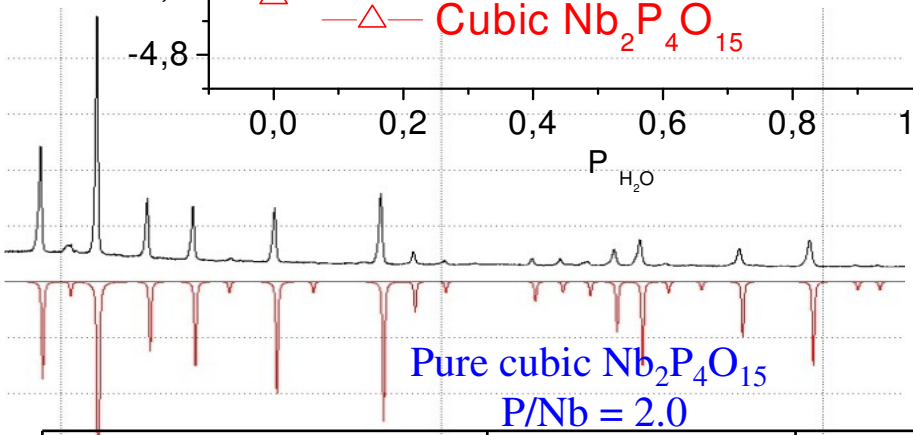
- Orthorhombic $Nb_{1.91}P_{2.82}O_{12}$
- Cubic $Nb_2P_4O_{15}$





Dependence of conductivity on P_{H2O}

- **Cubic $Nb_2P_4O_{15}$ stronger dependence**
  - **higher conductivity at higher P_{H2O}**



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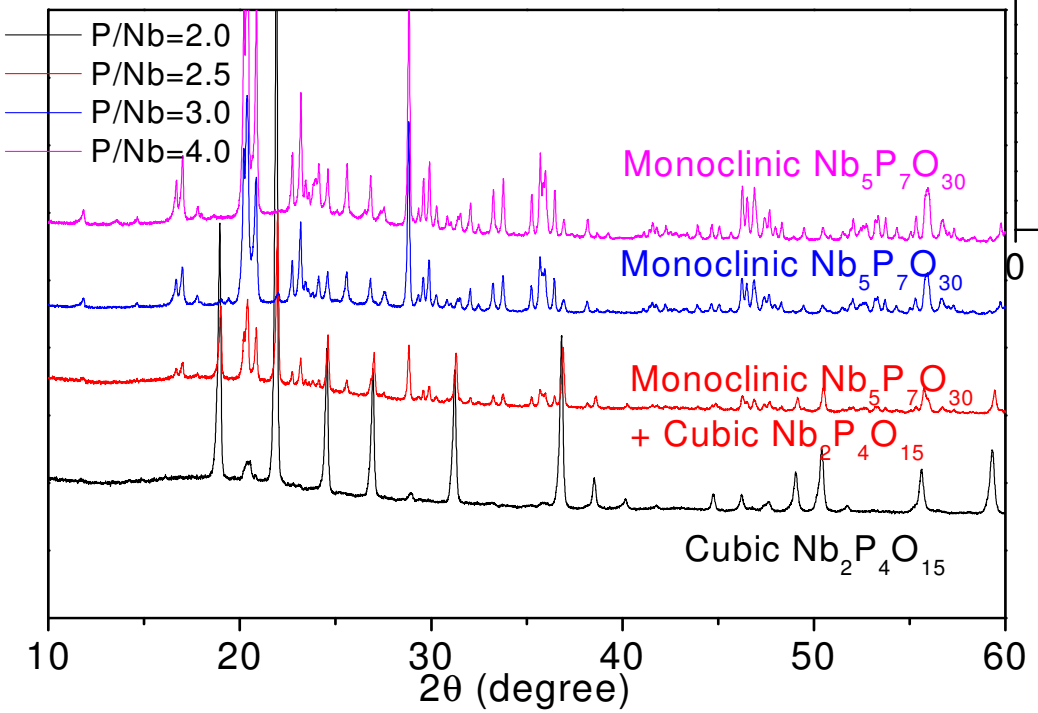
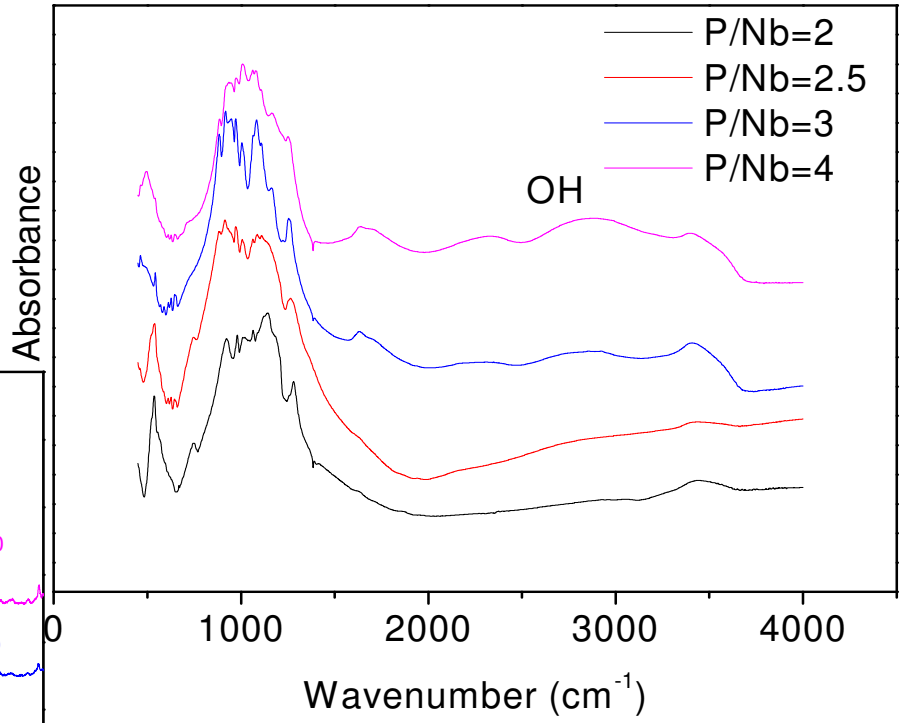
~~Monoclinic $Nb_5P_7O_{30}$~~	~~3,37~~	~~29.8~~	~~8,7~~	~~8,8~~	~~90~~	~~91.8~~	~~90~~	~~Favors at LT~~
Cubic $Nb_2P_4O_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT
Orthorhombic $Nb_{1,91}P_{2,82}O_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase Favors at LT

P/Nb Ratios

XRD – heat treatment at 650oC:

- P/Nb = 2.0: Cubic
  2.5: Cubic + monoclininc
  3-4: monoclinic





FTIR – heat treatment at 650°C

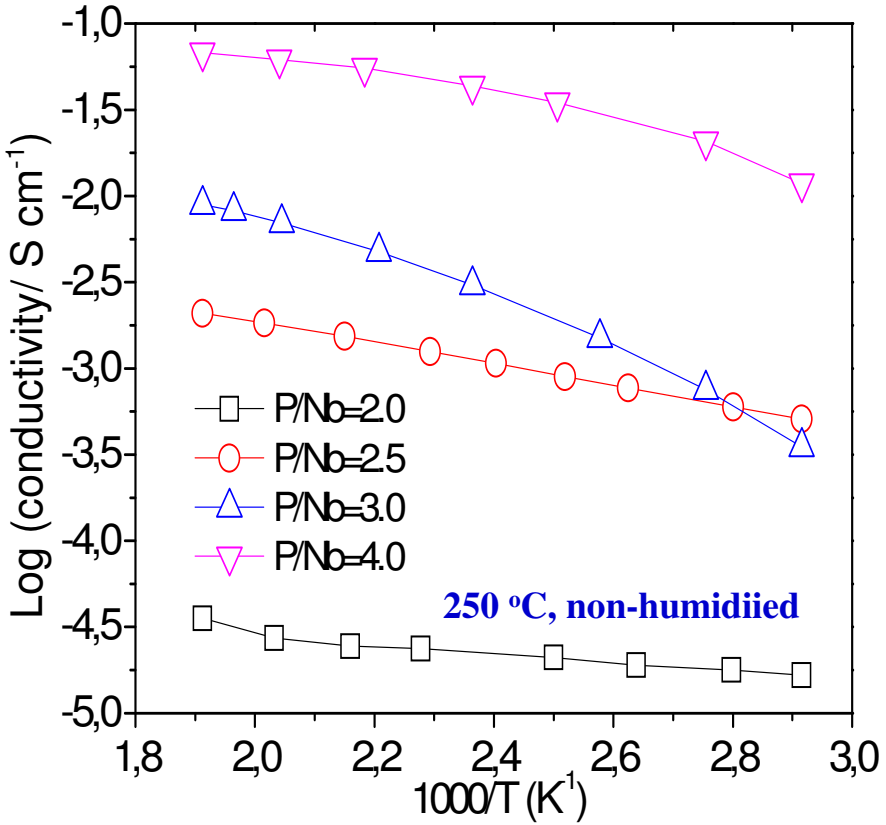
- P/Nb = 2.0: Low OH concentration
  2.5-4.0: higher OH content

	Theoretic. density, g/cm^3	Crystal parameters of unit cell						Notes
		a	b	c	α	β	γ	
Monoclinic $Nb_5P_7O_{30}$	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT, high P/Nb
Cubic $Nb_2P_4O_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT, low P/Nb
Orthorhombic $Nb_{1,91}P_{2,82}O_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase, Favors at LT

P/Nb Ratios

XRD & FTIR

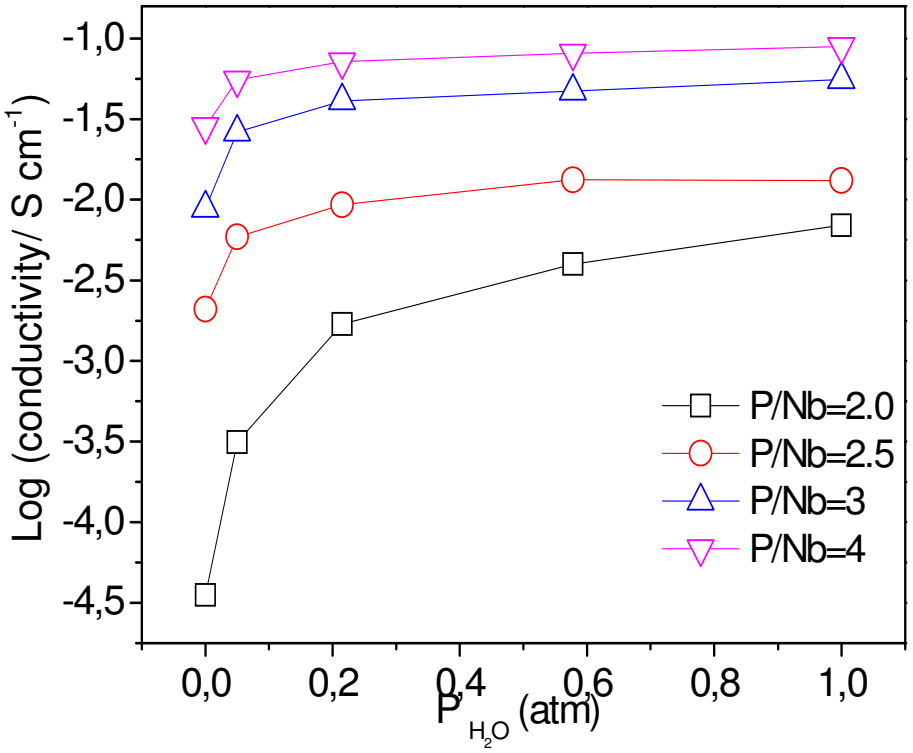
- P/Nb = 2.0: Cubic while low OH content
  2.5: Cubinc + monoclininc
  3-4: monoclinic but high OH content



Anhydrous conductivity

P/Nb= 4: High - Monoclinic + high OH
(amorphorous P_mO_n phase?)

P/Nb= 2: Low - Cubic + Low OH



Water vapor dependence

P/Nb= 4: Less - Monoclinic + high OH
(amorphorous P_mO_n phase?)

P/Nb= 2: More - Cubic + Low OH

Indium doping

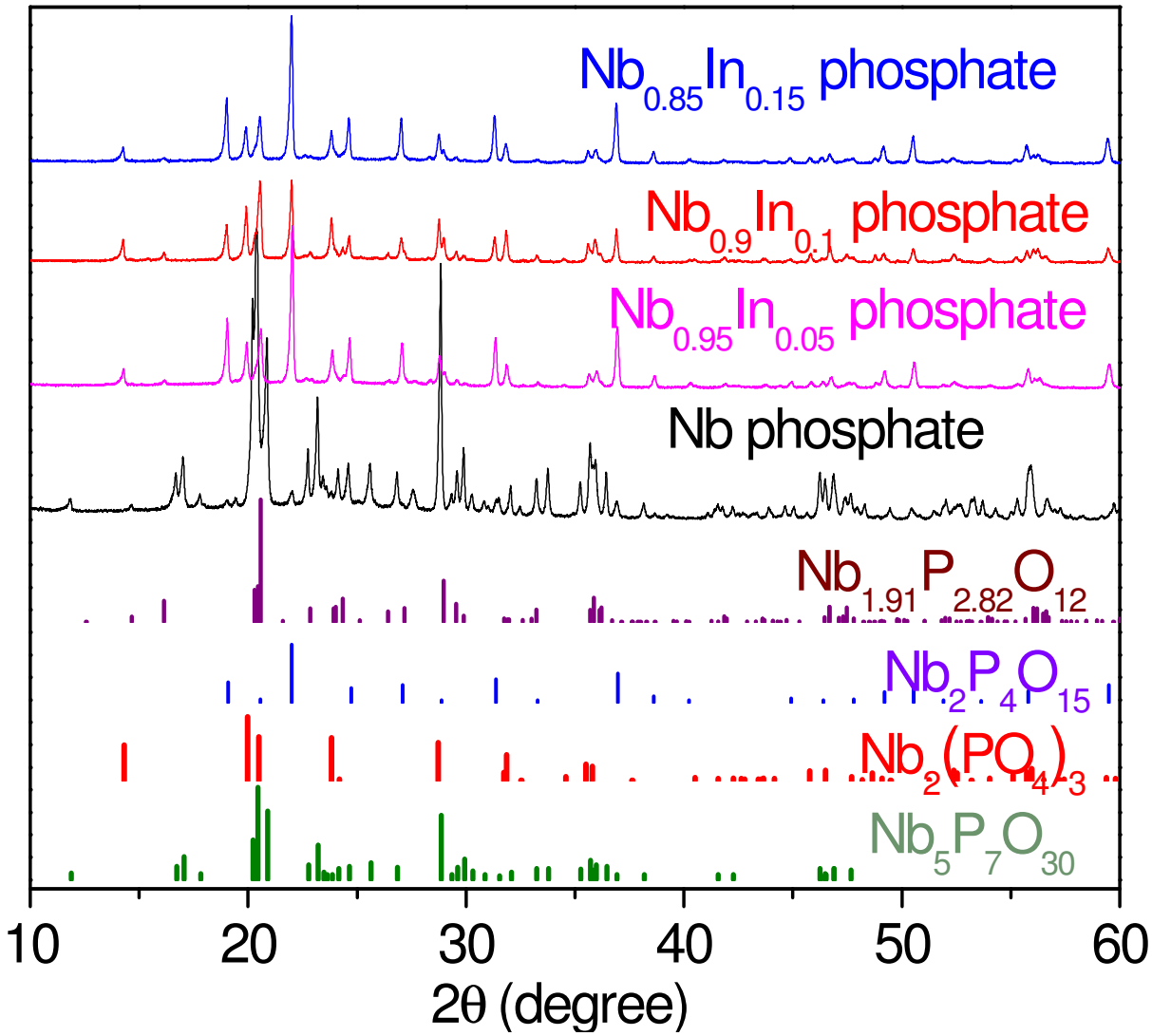
P/Nb = 3.0; 650°C

Pristine NbP:

Monoclinic $Nb_5P_7O_{30}$

Indium doped NbP:

Cubic $Nb_2P_4O_{15}$



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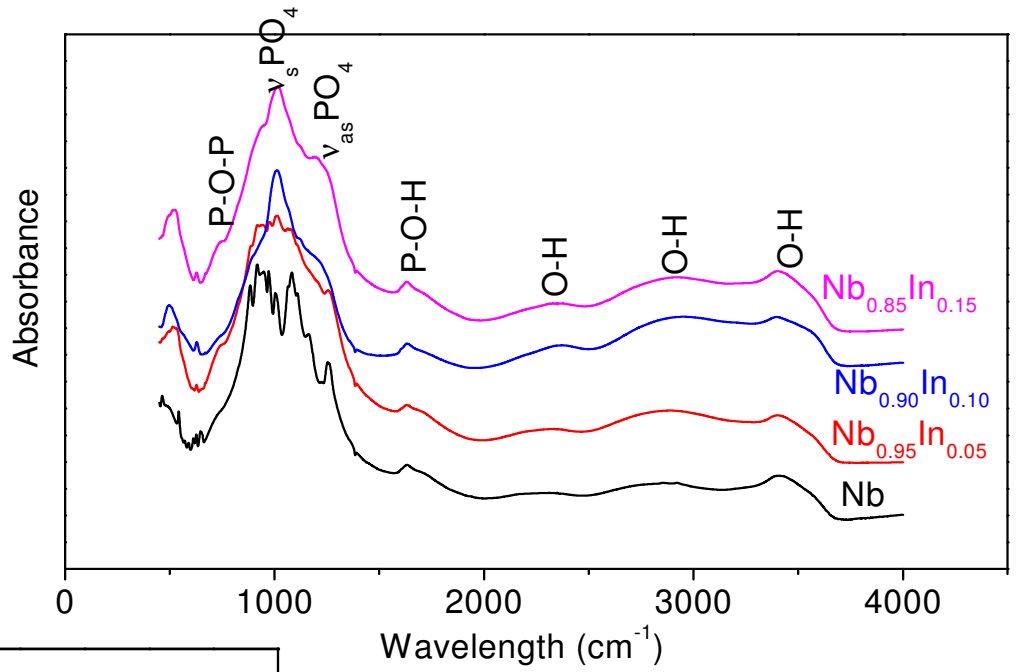
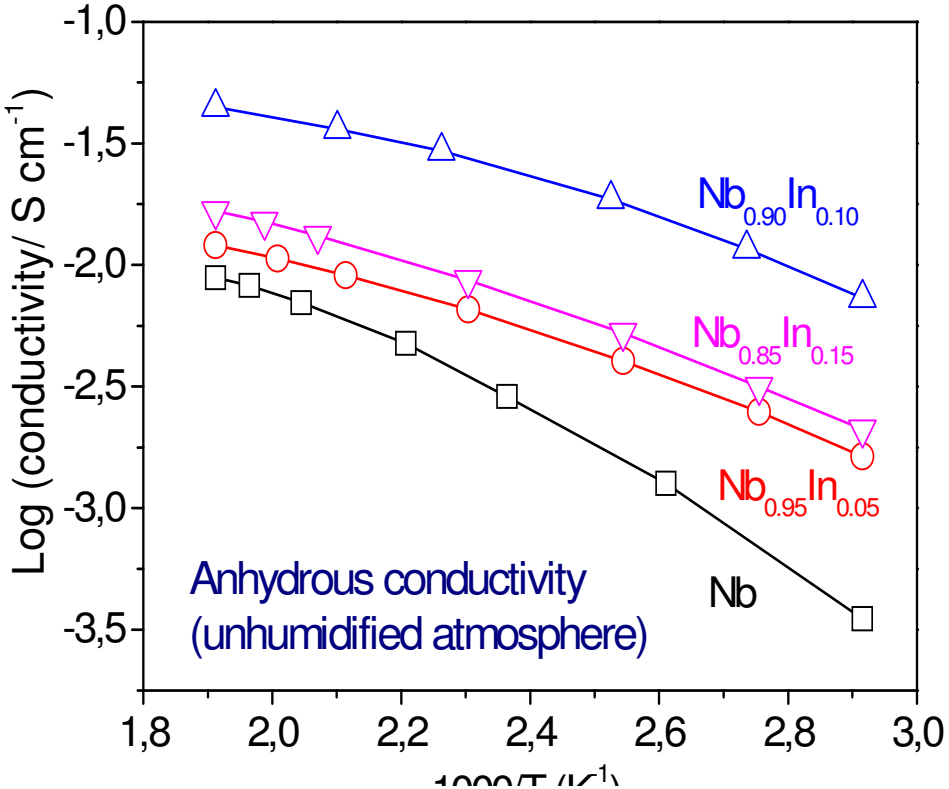
		a	b	c	α	β	γ	
Monoclinic $Nb_5P_7O_{30}$	3,37	29.8	8,7	8,8	90	91.8	90	Favors at LT, high P/Nb; NbP
Cubic $Nb_2P_4O_{15}$	3.15	8,0	8,0	8,0	90	90	90	Favors at HT, low P/Nb; In-NbP
Orthorhombic $Nb_{1,91}P_{2,82}O_{12}$	3,31	12.1	8,7	8,7	90	90	90	Minor phase in both NbP & In-NbP Favors at LT

Indium doping

- anhydrous conductivity

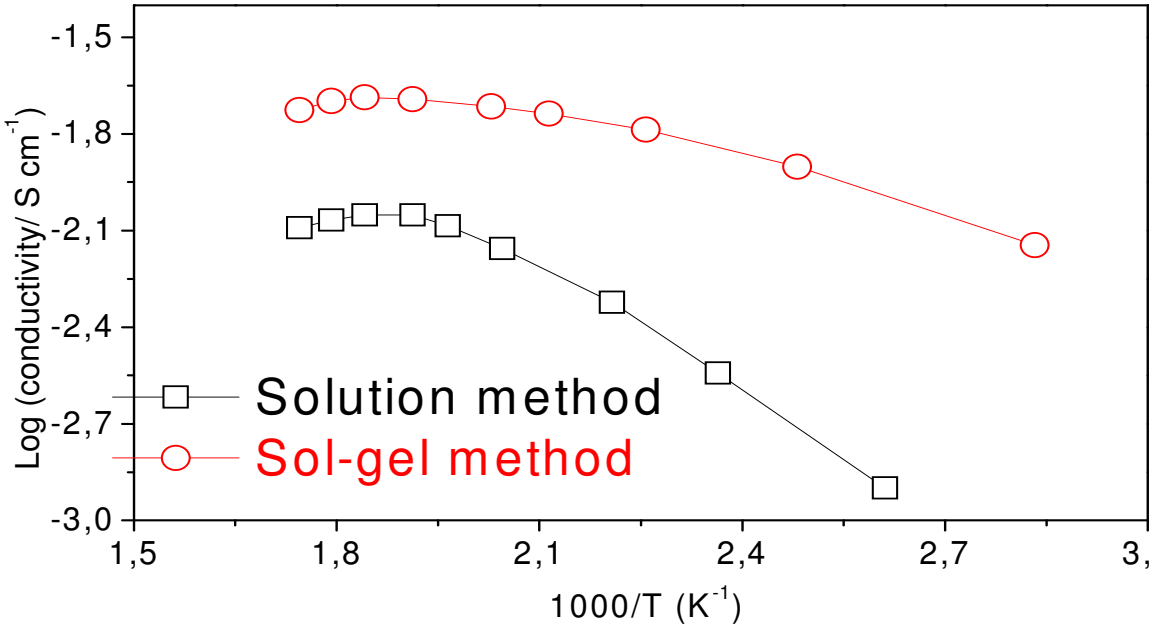
- Cubic $Nb_2P_4O_{15}$ favored
- OH groups enhanced/stabilized
  concentration & mobility

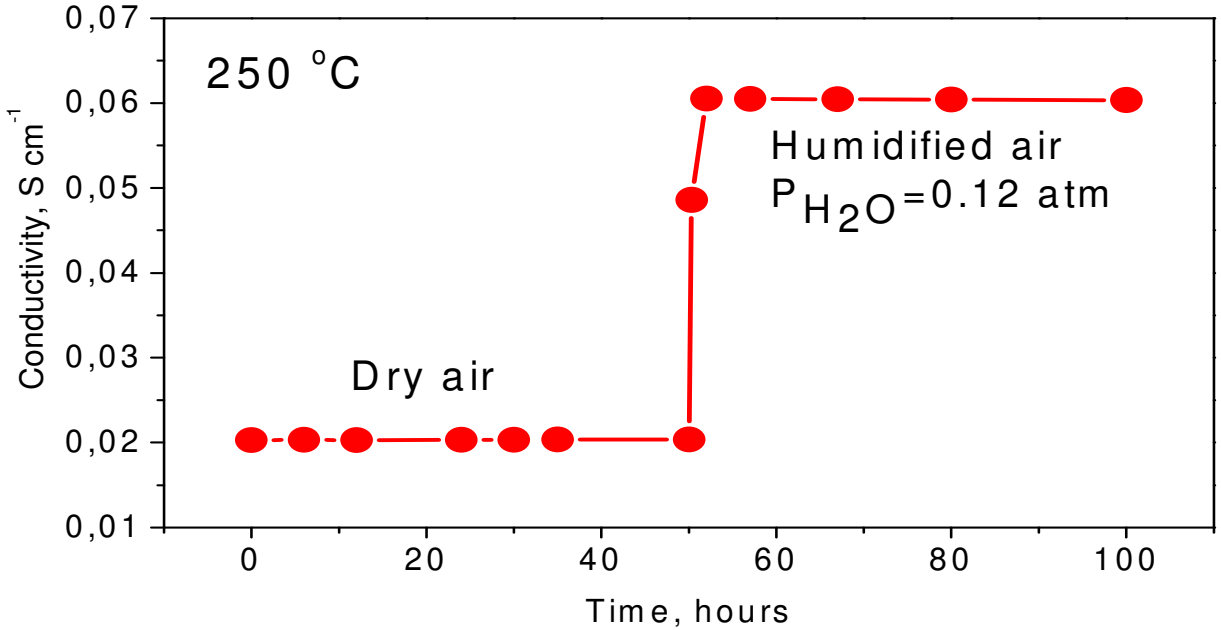


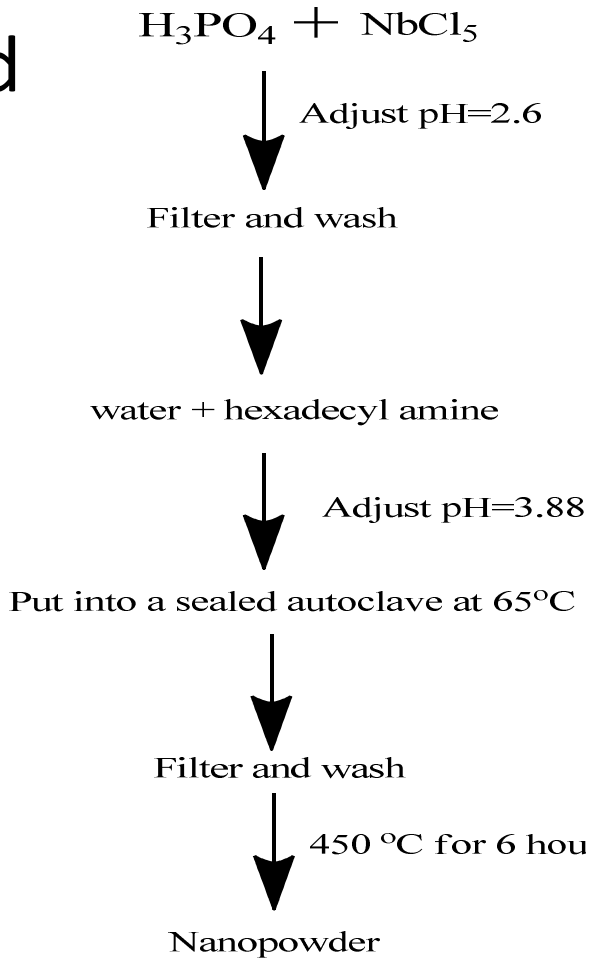


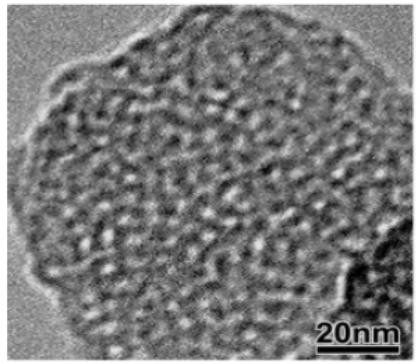
Un-humidified atmosphere
250°C

Morphology effects - sol-gel method





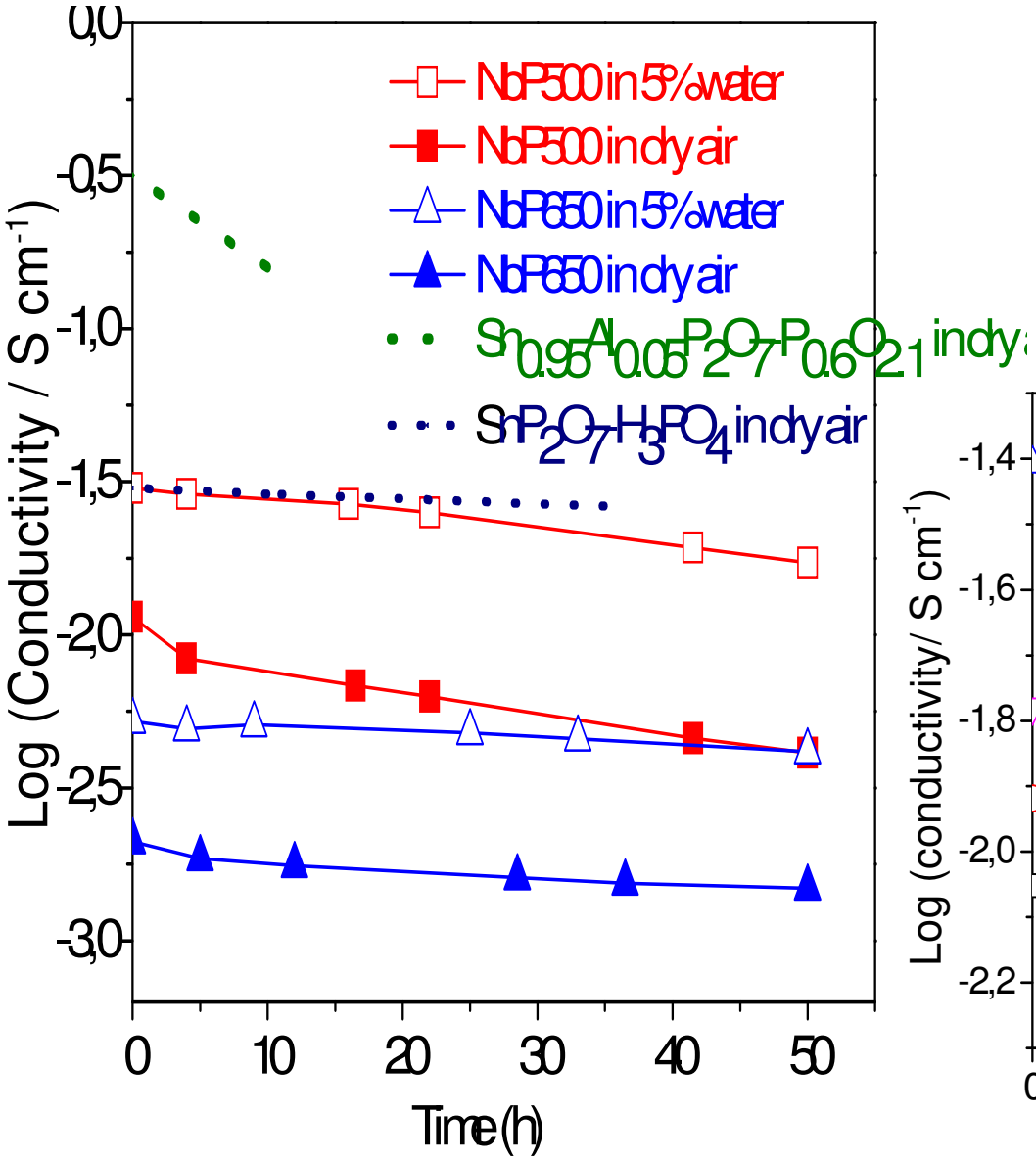




BET: 480 m^2 g^{-1}

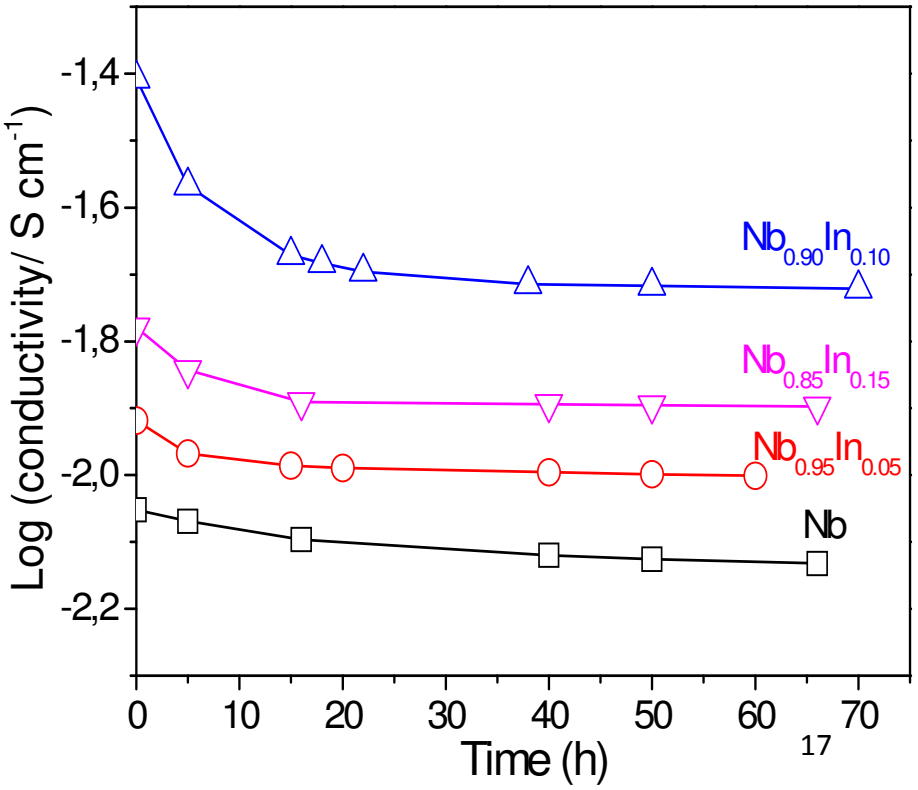
Heat Treatment Temperature

Under unhumidified atmosphere

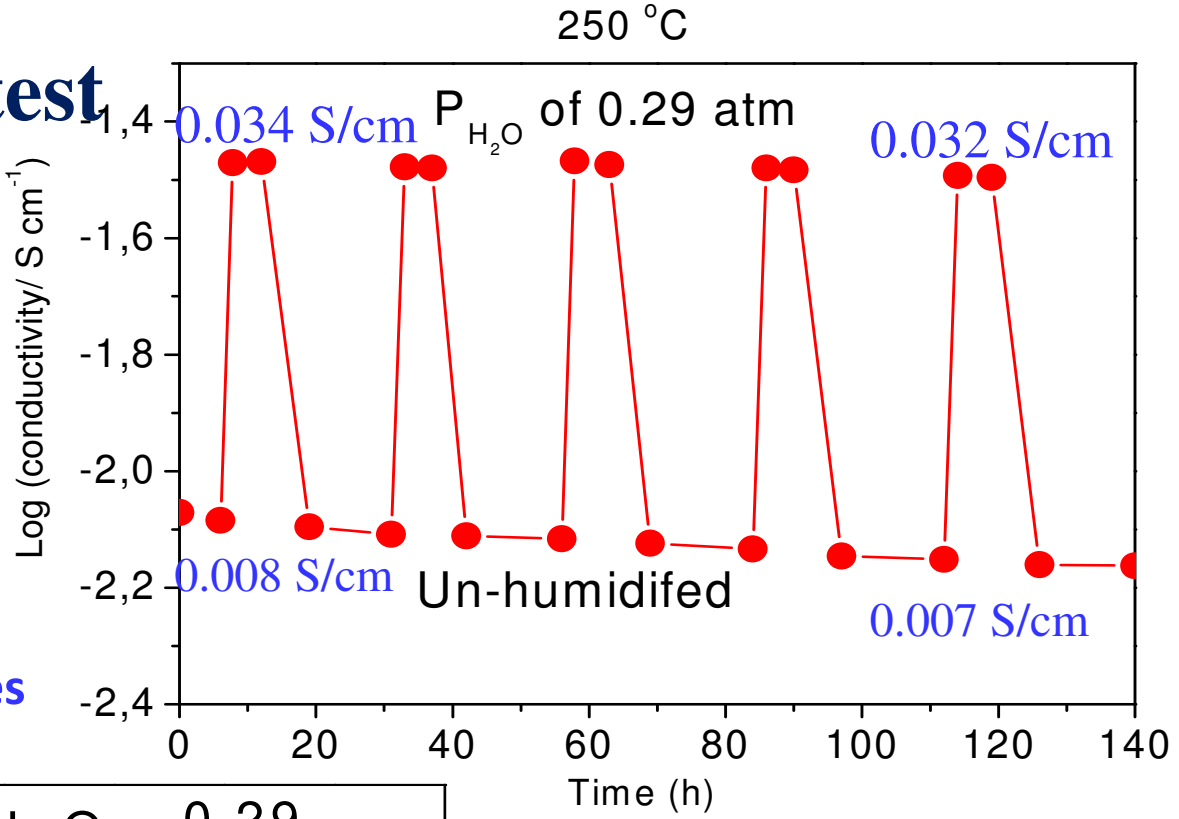


Heat treatment temperatures

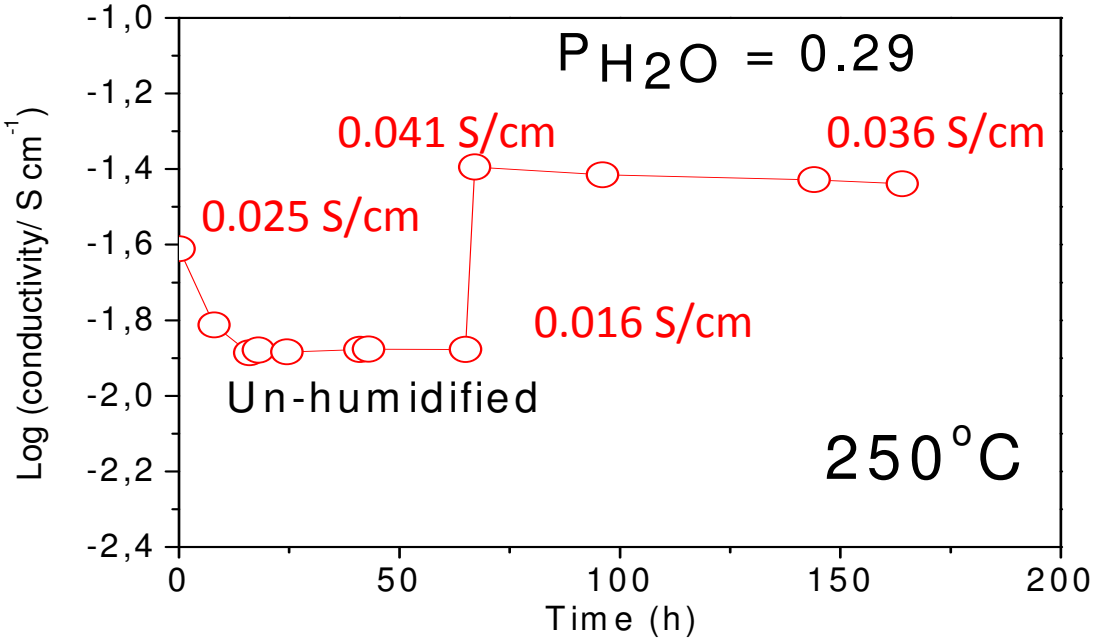
- better stability for 650 °C
- improved stability at 5% water vapor
- similar for other phosphates ?



Further stability test



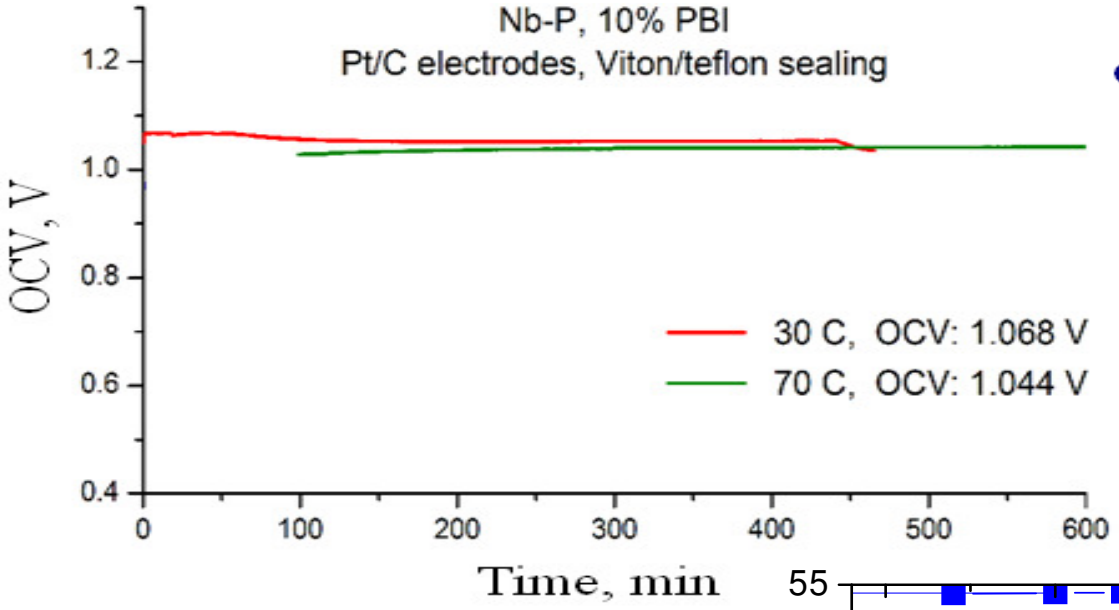
Under un-humidified and humidified atmospheres

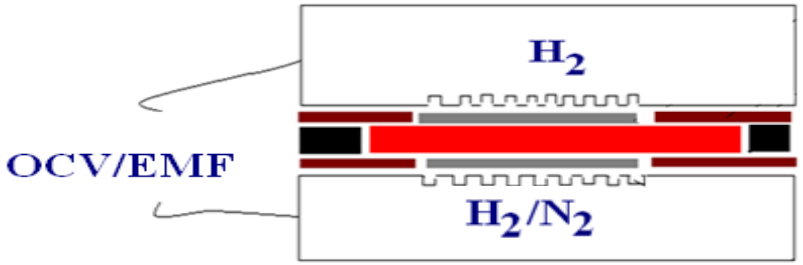


Daily humidity cycling

- $P_{H2O} = 0 \rightarrow 0.29 \rightarrow 0$ atm
- Humidified period: 3 hrs

OCV & EMF

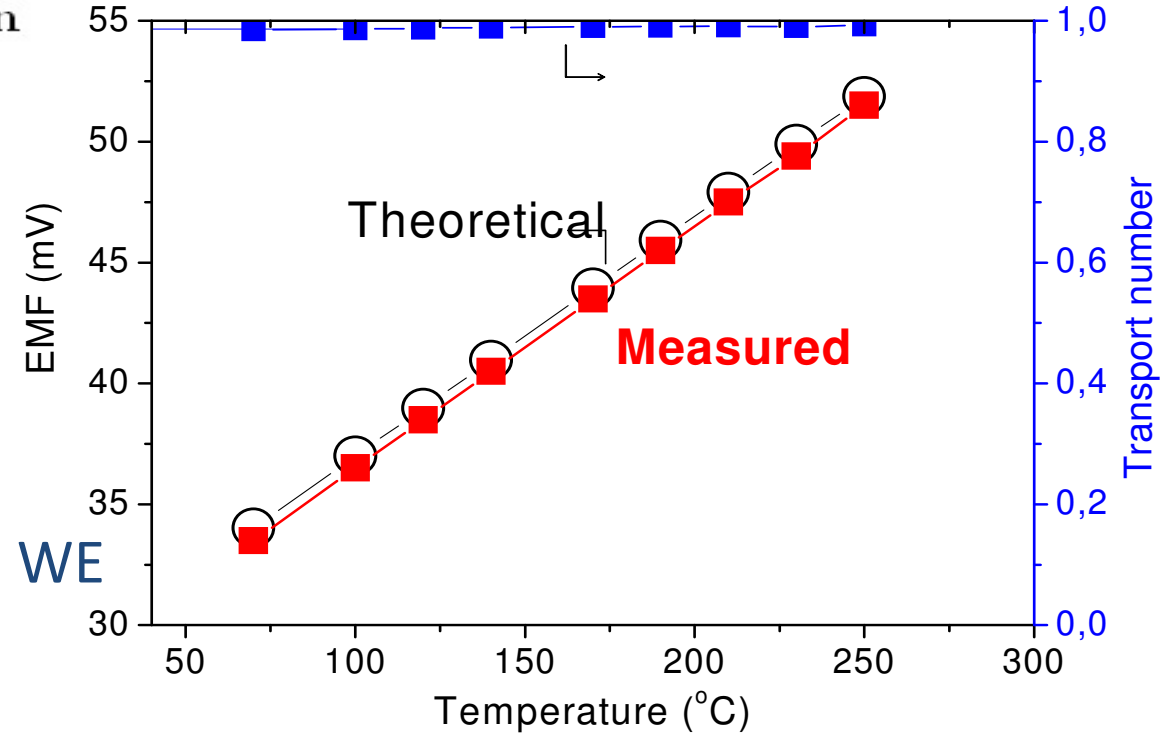




$$EMF = \frac{RT}{2F} \ln \left[\frac{P^1_{H_2}}{P^2_{H_2}} \right]$$

Following well the Nerst equation,
- indicating the conductivity protonic

$$\frac{P^1_{H_2}}{P^2_{H_2}} = 0.11$$



Efforts to assemble FC and WE cells are under the way.

Acknowledgements

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  Danish-Chinese Centre of Proton Conducting Systems
- **Danish Agency for Science, Technology and Innovationan**
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- **Danish Public Service Obligations (ForskEL programme)**
  HOT-MEA Consortium