FLORIDA SOLAR ENERGY CENTER

X-Ray Photoelectron Investigation of Phosphotungstic Acid as a Proton-Conducting Medium in Solid Polymer Electrolytes

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Tungsten trioxide, WO_3

- Melting point: 1473 K
- Insoluble in mineral acids
- Soluble in alkali

  $$WO_3 + 2NaOH \rightarrow Na_2WO_4 + H_2O$$

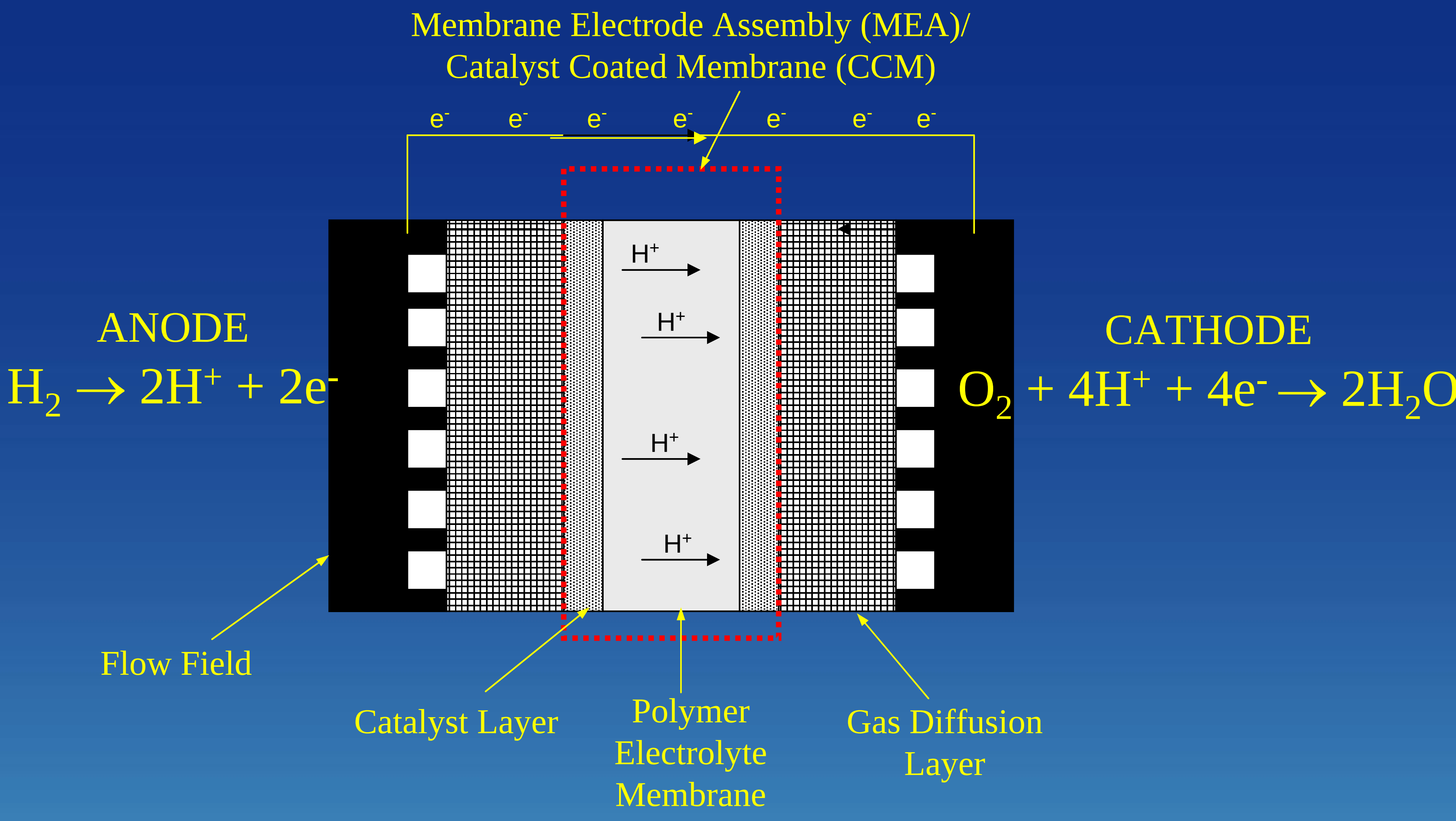
- Formation of phosphotungstic acid, PTA:

  $$H_3PO_4 + 12WO_3 \rightarrow H_3PW_{12}O_{40}\text{-}xH_2O$$

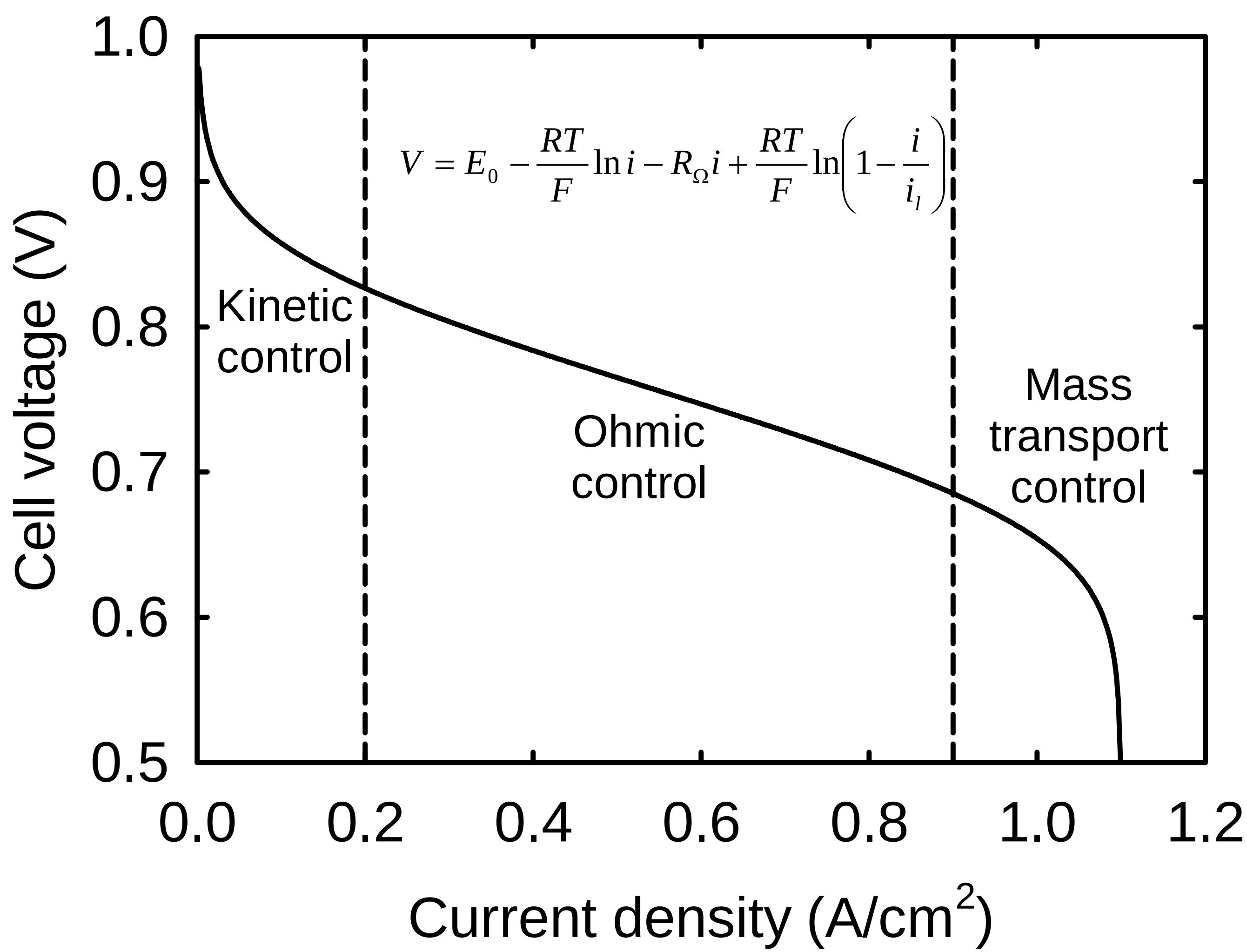
Outline

- PEM fuel cell function
- Conductivity in polymer electrolytes
- Effect of PTA on sulfonic acid polymer membrane conductivity
- XPS observation of W chemical shifts
- Relating chemical shift data to hydration environment
- Thermogravimetry
- Conclusion
- Future work

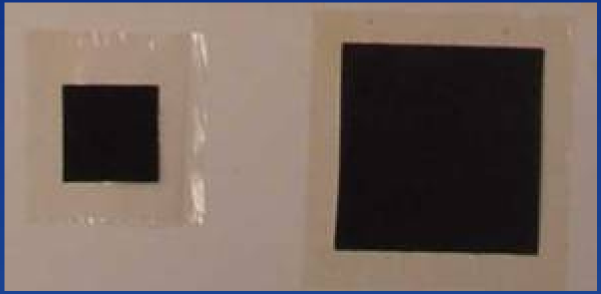
Polymer Electrolyte Membrane Fuel Cell



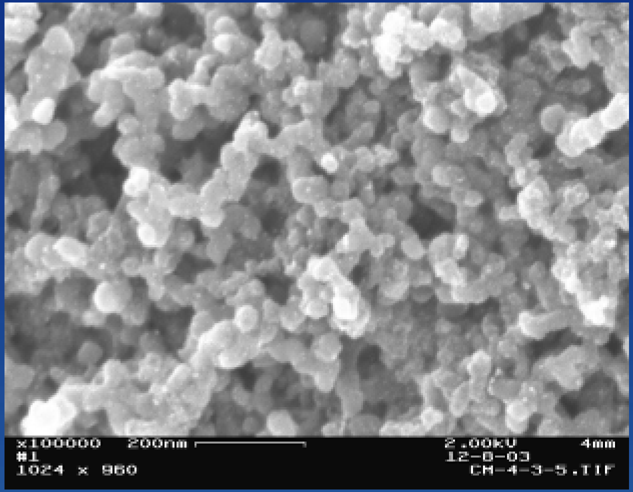
Typical Current-Voltage curve for a PEM fuel cell



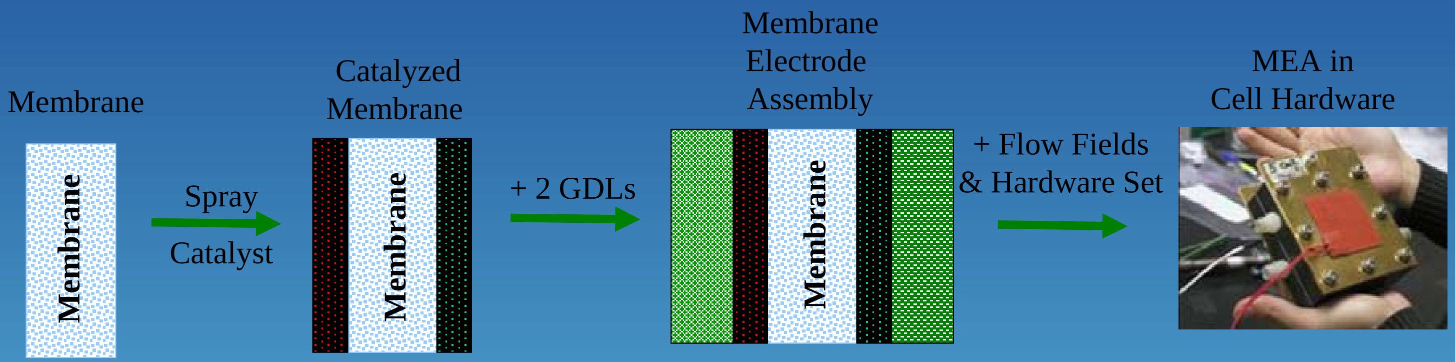
Membrane Electrode Assembly- the heart of a PEM fuel cell



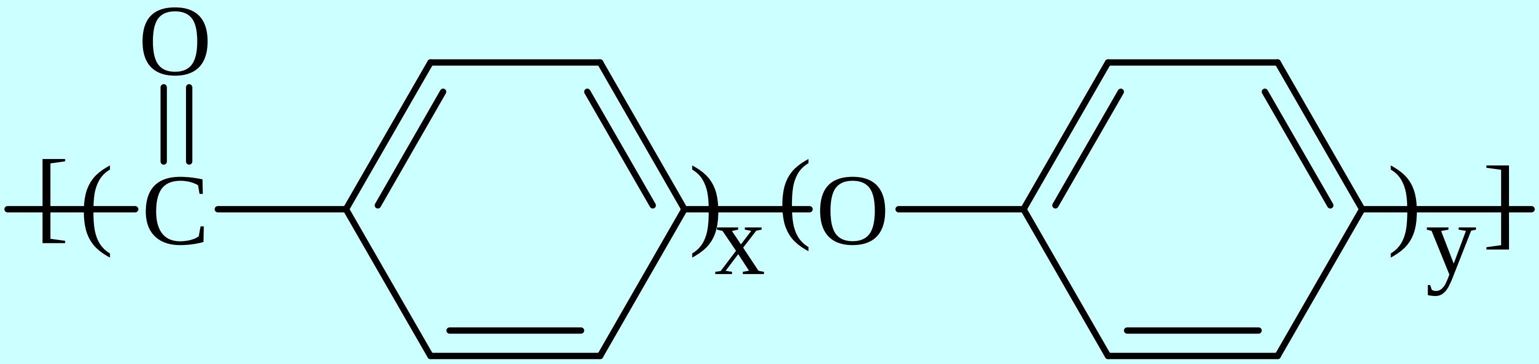
Polymer membranes with catalyst ink



sprayed catalyst ink layer

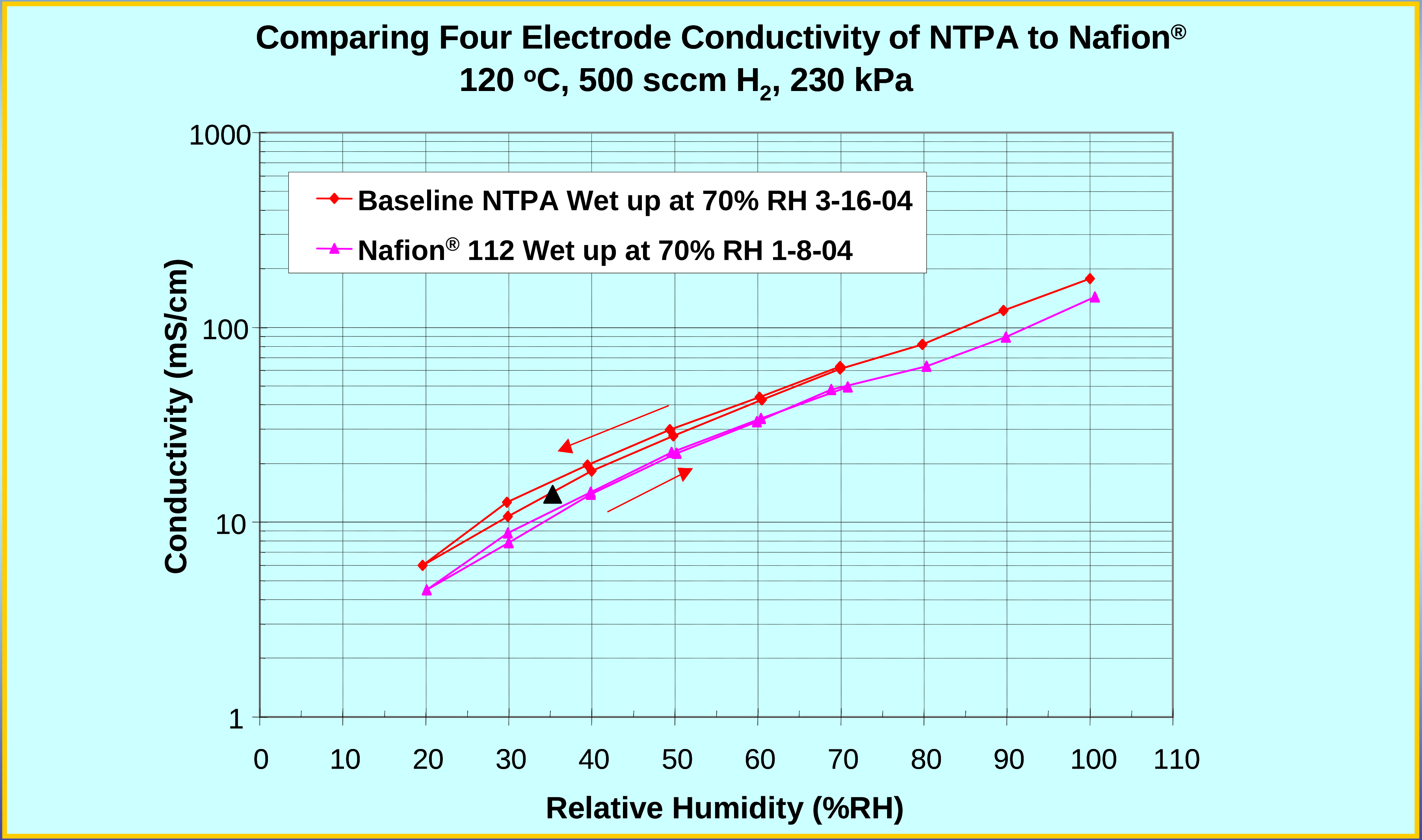


Base Polymer of interest: PEEK and PEKK



poly(aryletherketone)

Previous work on Nafion® 112 and PTA composite

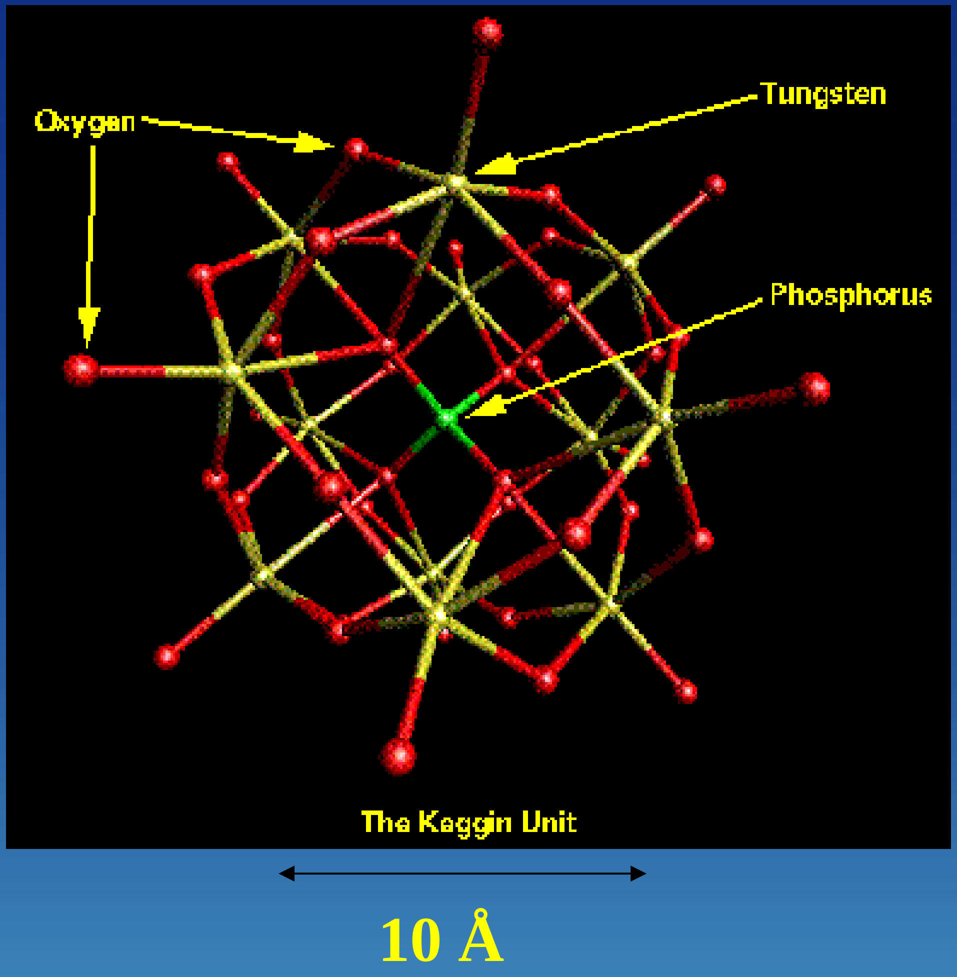


Solid Acid Additives for Membrane Modification

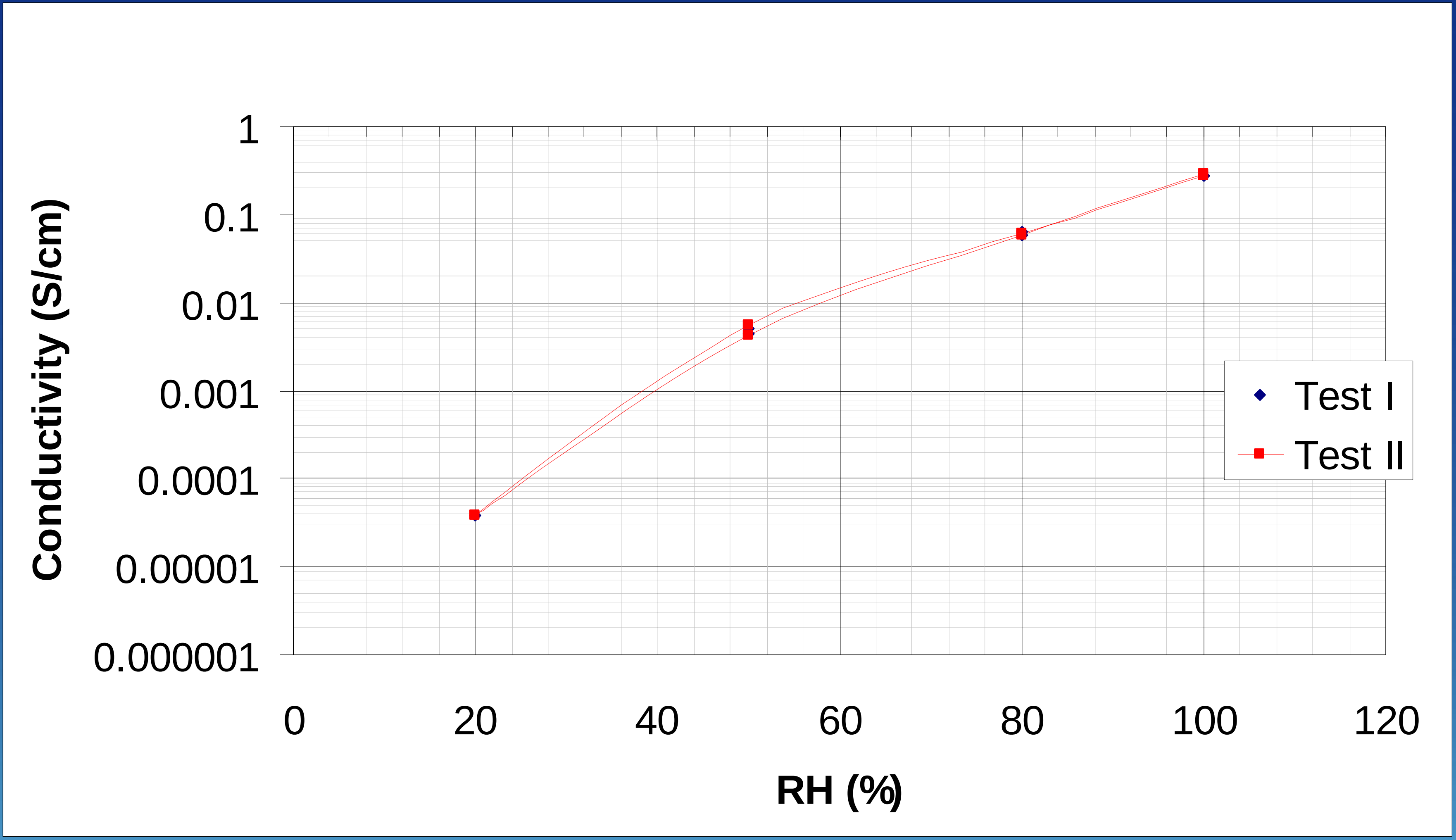
Keggin structure

Phosphotungstic acid (PTA)

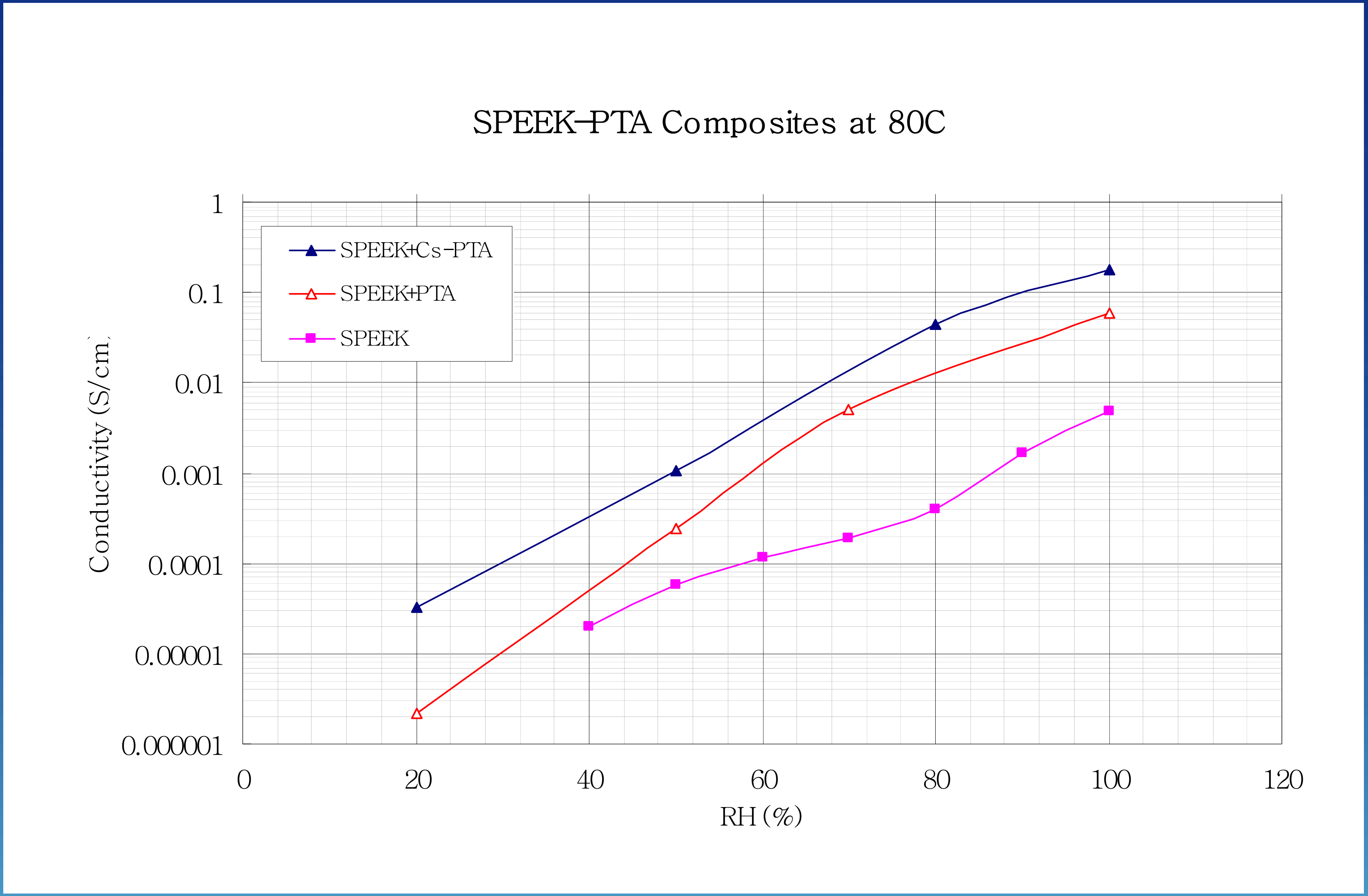
$12WO_3 * H_3PO_4 * 24H_2O$



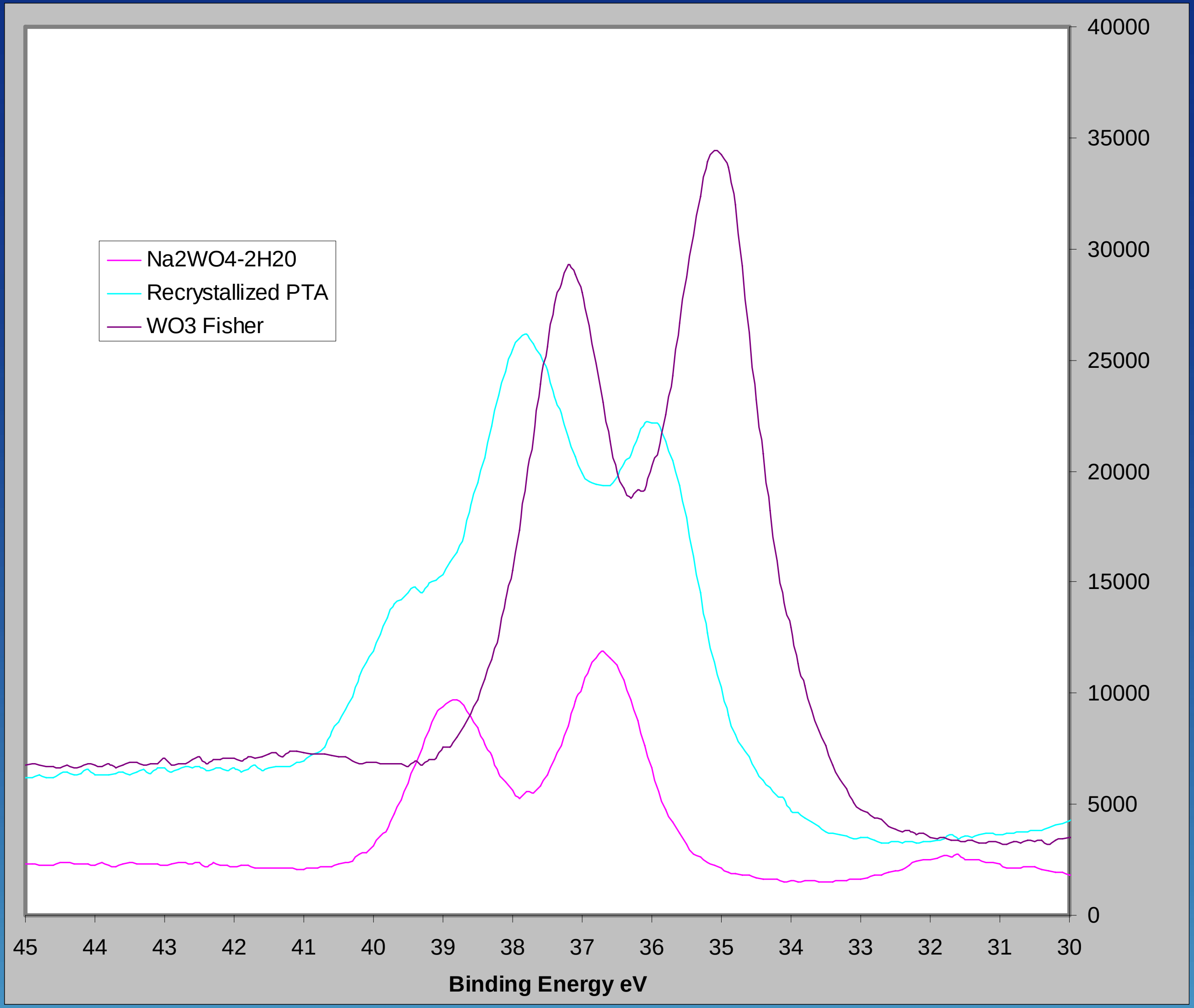
Conductivity vs RH for SPEEK/PTA composite membrane



Effect of Cs+ treatment on PTA/SPEEK composites



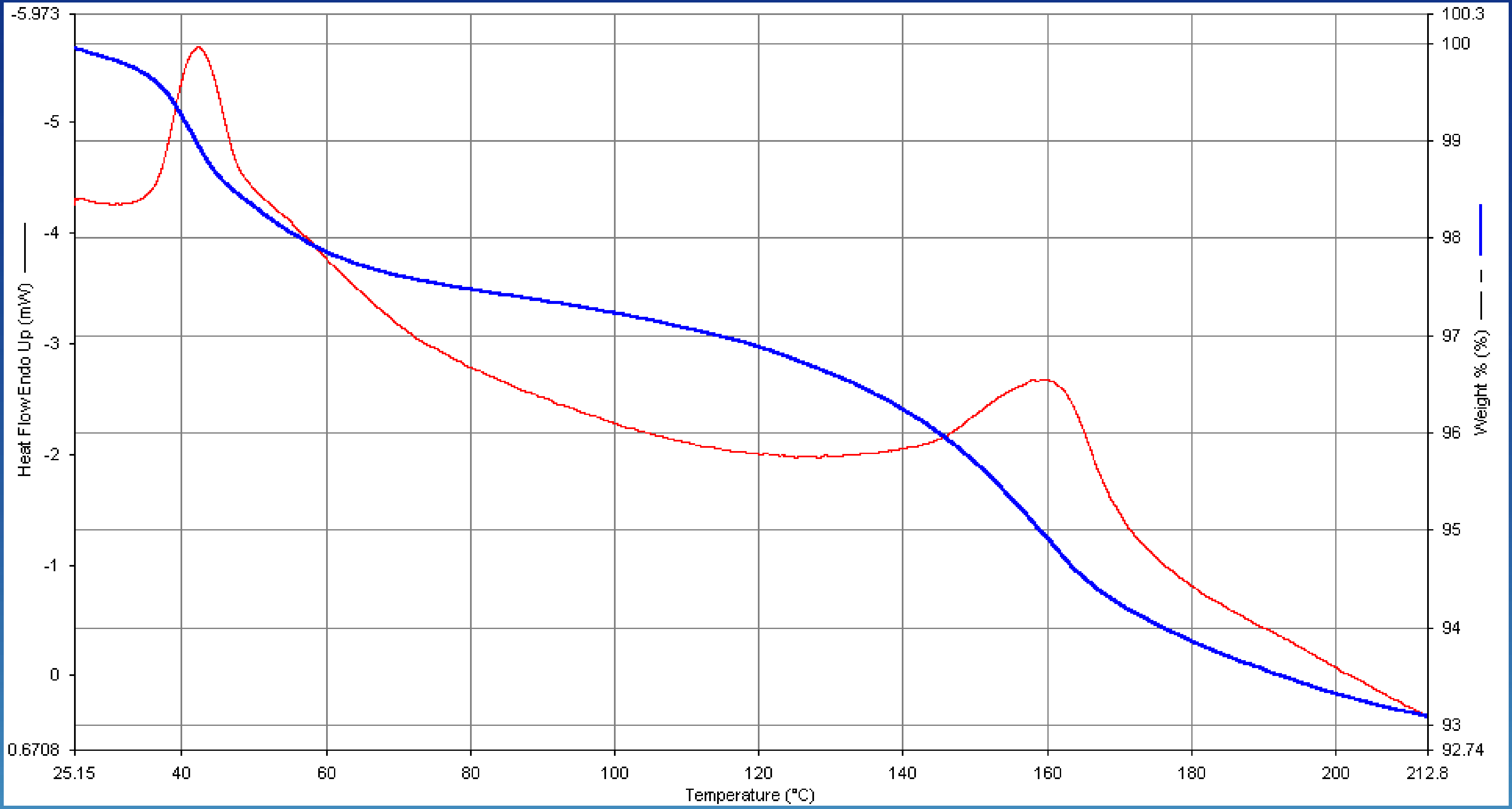
Representative W4f spectra



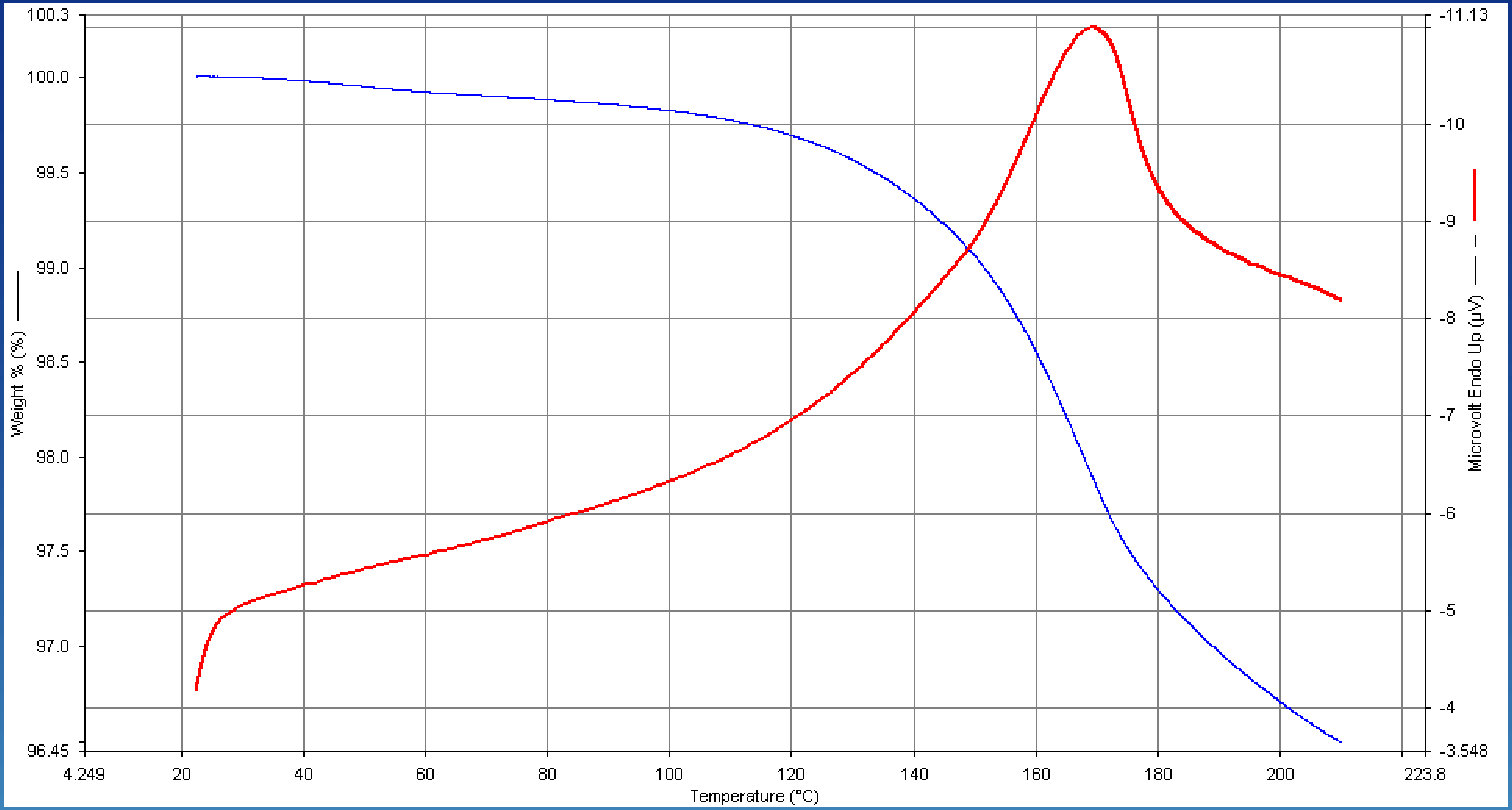
Summary of $W4f_{7/2}$ data

Sample	Binding Energy (eV)
WO_3	35.1
PTA + Cs_2CO_3	35.4
PTA/Cs^+/H_2SO_4	35.6
SPEEK/PTA	35.7
PTA + CsCl	35.8
Na_3PTA	35.9
PTA-6H_2O	36.0
PTA-EtOH/DMF	36.2
PTA (anhydrous)	36.2
PTA – 24H_2O (recrystallized)	37.8, 36.0
Na_2WO_4-2H_2O	36.7
Cs_2WO_4 (anhydrous)	37.3, 35.3
PTA--24H_2O (commercial A)	37.5
PTA--24H_2O (commercial B)	37.6
Cs_2WO_4-2H_2O	37.7

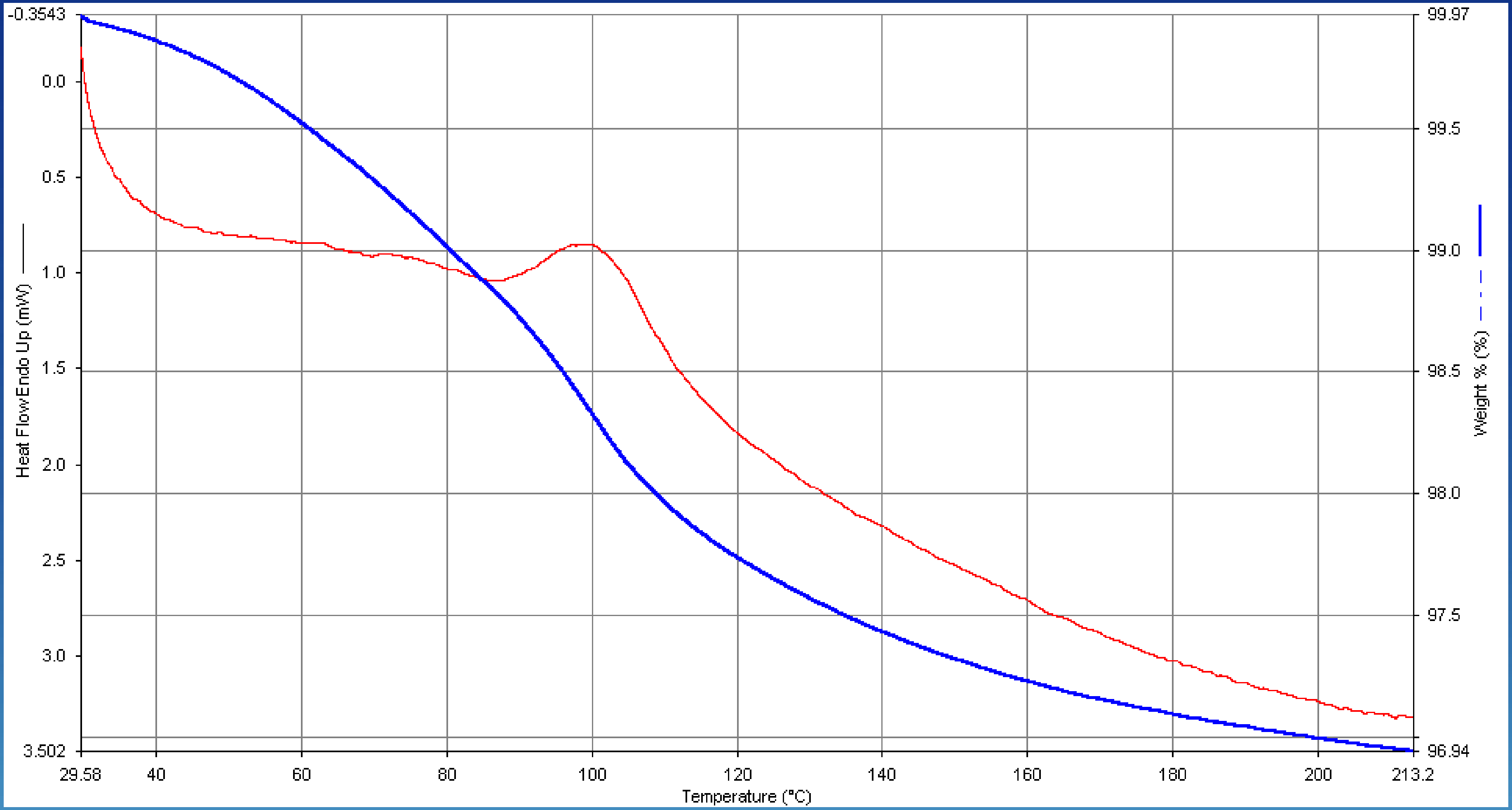
Weight loss thermogram for $PTA\text{-}24H_2O$



Weight loss thermogram for $PTA\text{-}6H_2O$



Weight loss thermogram for PTA treated with Cs_2CO_3



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Cs_2WO_4 (anhydrous)	37.3, 35.3
PTA-24H_2O (commercial A)	37.5
PTA-24H_2O (commercial B)	37.6
Cs_2WO_4-2H_2O	37.7

Conclusion

- Cs^+ exchange improves conductivity of SPEEK/PTA composite membranes.
- W chemical shift related to O-bonding geometry (octahedral vs tetrahedral) and waters of hydration.
- Cs^+ treatment lowers PTA water content and its enthalpy of hydration.
- Cs^+ functions by destabilizing waters of hydration, rendering them more mobile and better able to conduct protons.

Future Work

- XRD of PTA vs water content
- IR analysis of retained hydrogen stretching frequencies
- Obtaining conductivity vs RH curves at temperatures on either side of the TGA water transition.
- Fabricating Pt//SPEEK/PTA//Pt membrane electrode assemblies and deriving fuel cell current voltage curve