

Development of High Temperature Proton Exchange Membrane Electrolytes

Clovis A. LINKOUS

Florida Solar Energy Center

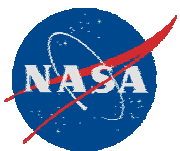
University of Central Florida

Cocoa, Florida, USA

E-mail: calink@fsec.ucf.edu

Start Date = November '04

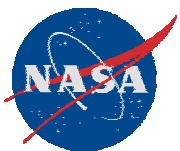
Planned Completion = December '06



Research Goals and Objectives

Develop proton-conducting solid electrolytes possessing the following characteristics:

- Proton conductivity in excess of 0.1 S/cm
- Temperature stability at $T > 125\text{ }^{\circ}\text{C}$
- Reduced humidity dependence on water saturating conditions ($< 25\%$ relative humidity)



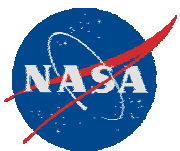
Relevance to Current State-of-the-Art

- Fuel Cell specific power ~ 100 W/kg
- Proton Exchange Membrane (PEM) conductivities ~ 0.1 Siemens/cm

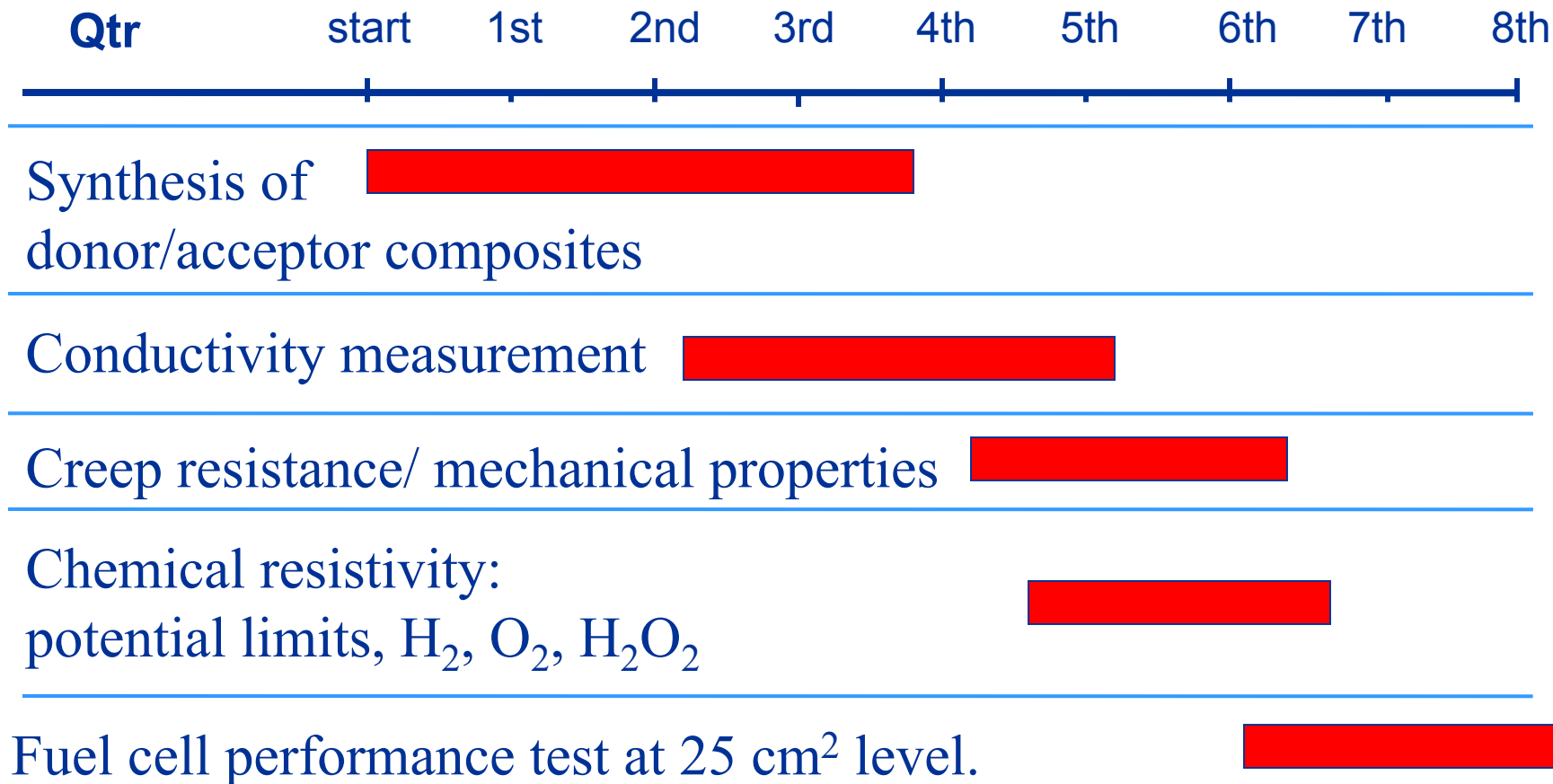
Relevance to NASA

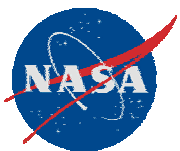
Task VII – Hydrogen Powered Aeropropulsion

- Improve power density of fuel cells
- Renewable power generation



Budget, Schedule and Deliverables





Anticipated Technology End Use

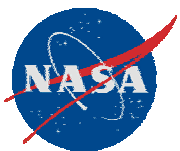
Vehicle Systems Program

-New Aircraft Energy Sources and Management focus area

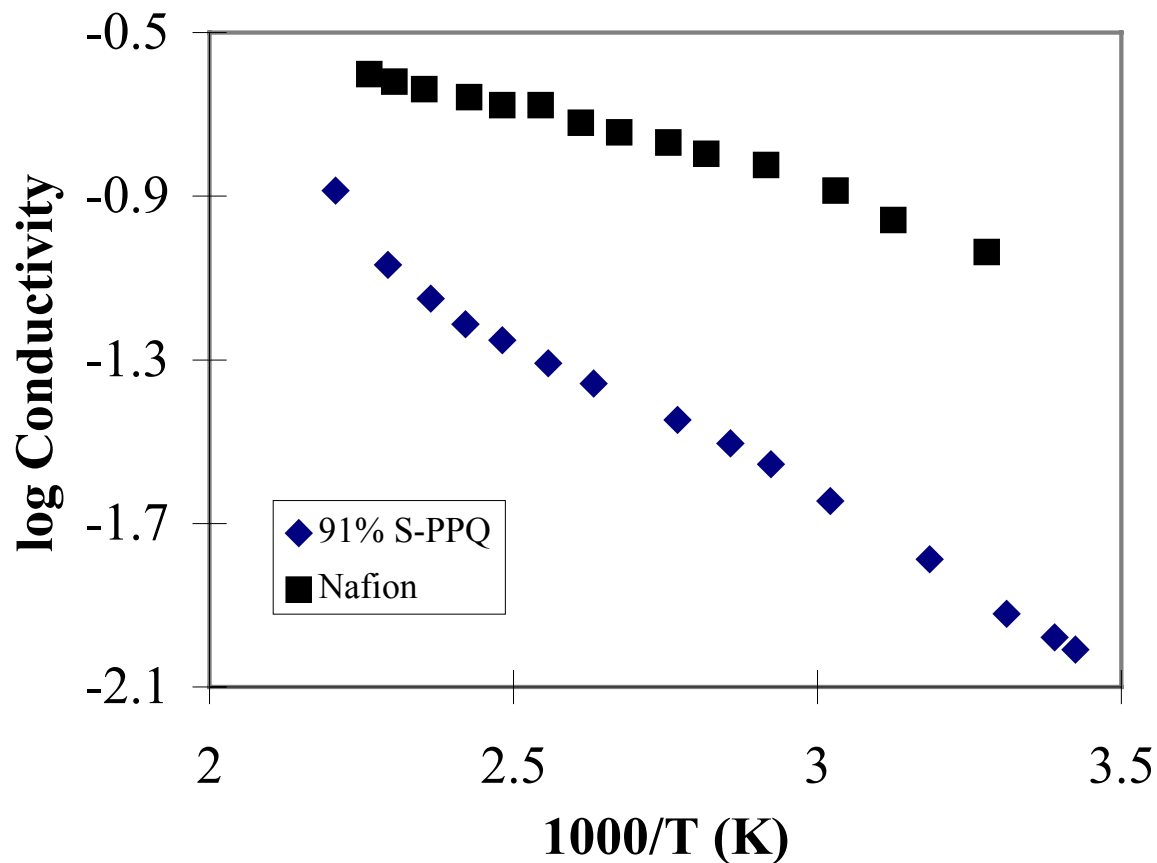
-LEAP (Low Emission Alternative Power) project

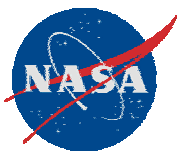
-AFCPS (Aircraft Fuel Cell Power System): “Develop and demonstrate fuel cell-based power system.”

- focus: Regenerative PEM fuel cell development for HALE (High Altitude Long Endurance) solar electric aircraft
- longer-term: High temperature PEM materials ($> 125\text{ }^{\circ}\text{C}$, 25% relative humidity), secondary and primary



Rationale: Effect of Temperature on Conductivity for Membrane Electrolytes





Structure of Hexagonal Boron Nitride

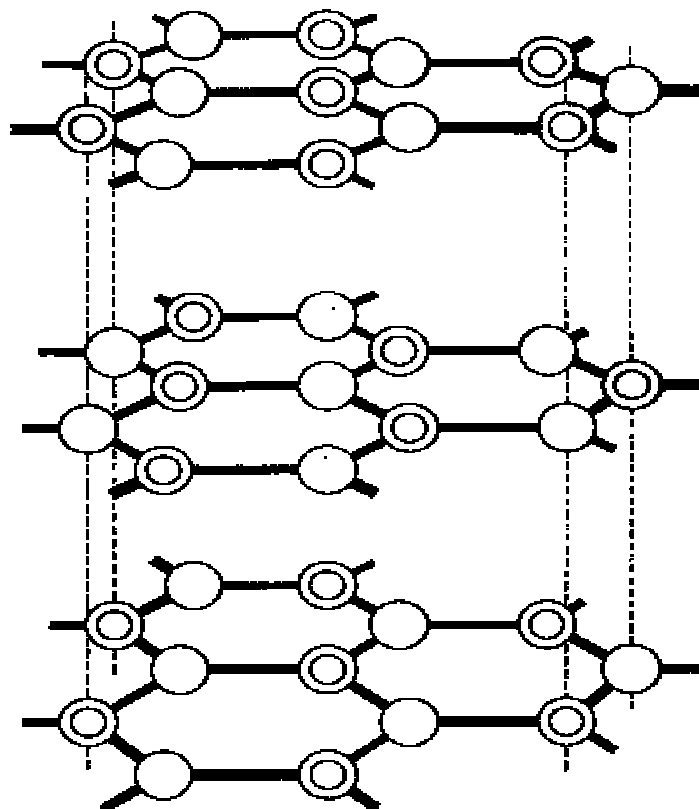
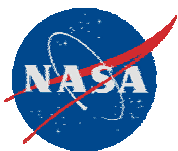


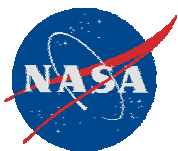
Fig. VI-1: Layer Arrangement in hexagonal Boron Nitride

K. Niedenzu and J.W. Dawson, Boron-Nitrogen Compounds, Academic Press, New York, 1965



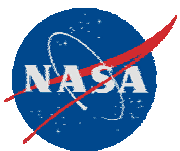
Accomplishments and Results

- hexagonal BN used a matrix for proton donors (Bronsted acids)
- No clear evidence of intercalation was detected
- h-BN found to be inert to H_3PO_4 and H_2SO_4 ; earlier mass gains due to capillary uptake
- Similar behavior found for BC and SiN
- Proton conductivity measurement of BN- H_3PO_4 composites in progress

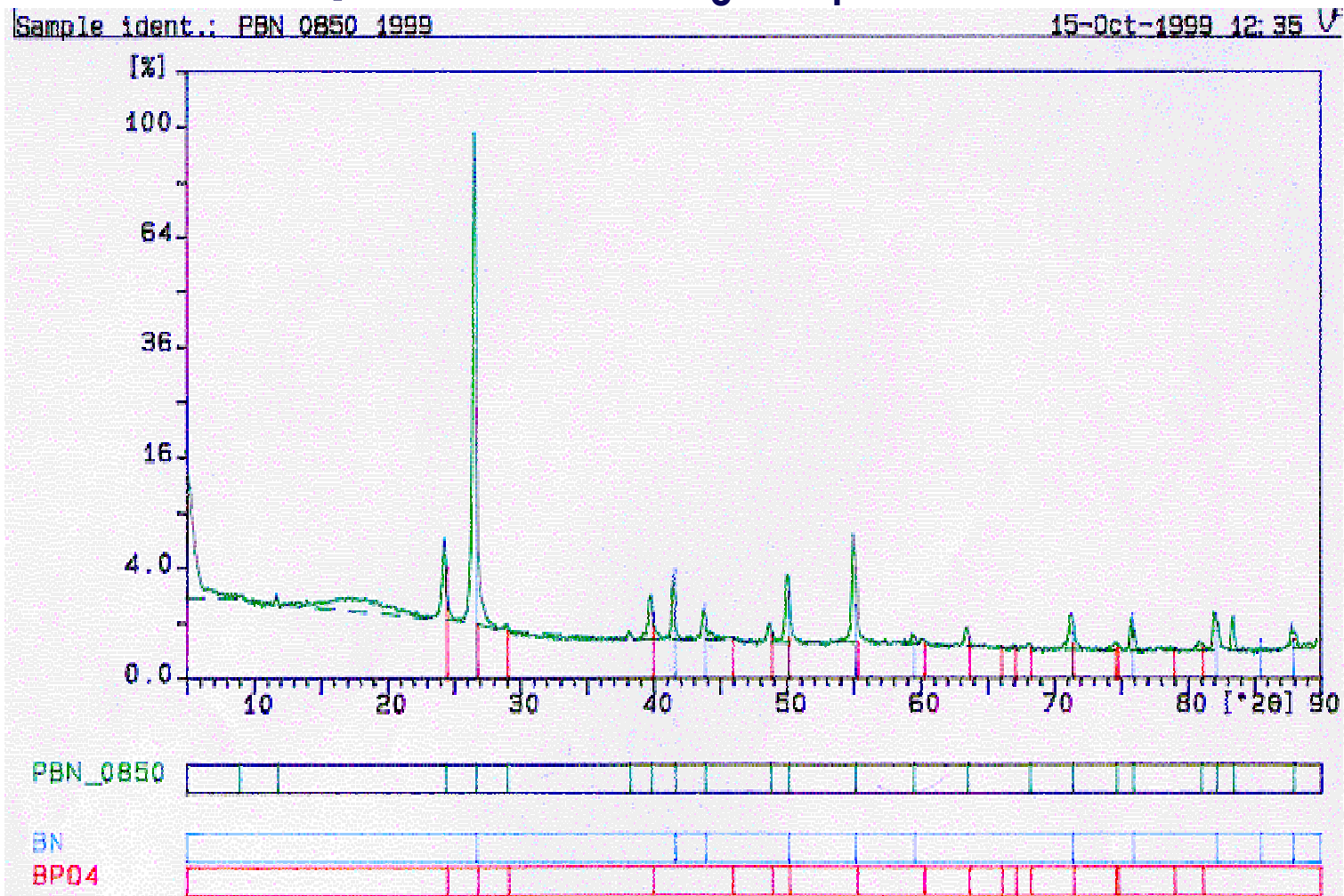


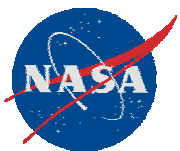
Acid Stability of h-BN

<u>Acid</u>	<u>% weight change after 24 h exposure</u>	<u>Acid</u>	<u>% weight change after 24 h exposure</u>
HCl	-0.54	HNO ₃	-0.81
HCl (1 week)	-1.50	HNO ₃ (11% NO ₂)	-0.763
HCl (3 h, 80° C)	-2.51	CH ₃ SO ₃ H	-0.80
HBr	-0.97	CF ₃ SO ₃ H	-0.40
HI	-0.96	CF ₃ COOH	-0.12
H ₂ SO ₄	+42.0	NH ₄ OH	+0.70
H ₂ SO ₄ (30% SO ₃)	+88.7	NaOH (8.0 M)	+5.5
H ₃ PO ₄	+36.1	H ₂ O	-0.57
HClO ₄	-0.10		

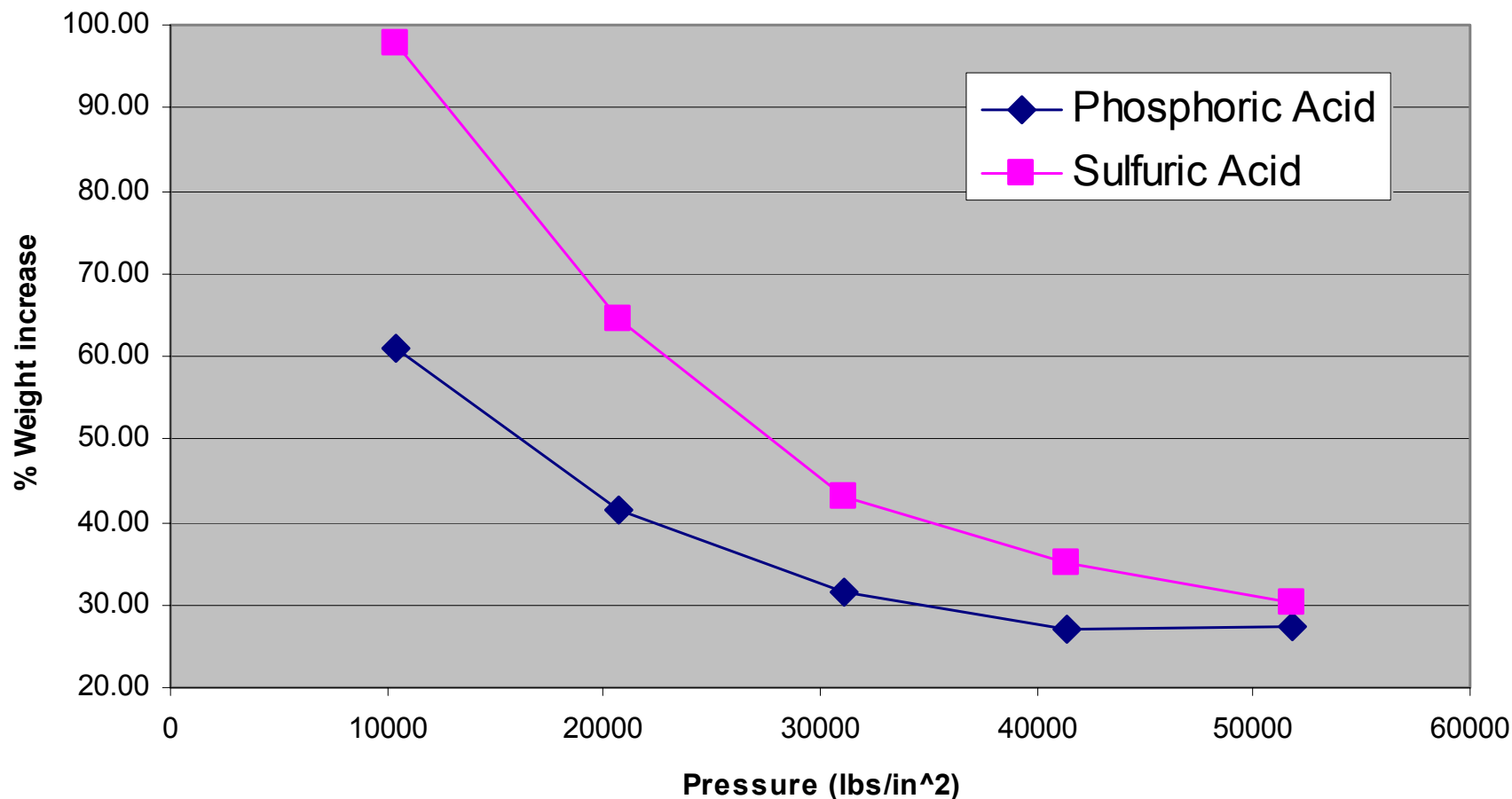


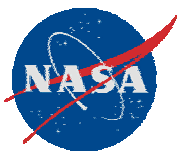
XRD Spectrum of H_3PO_4 -treated h-BN



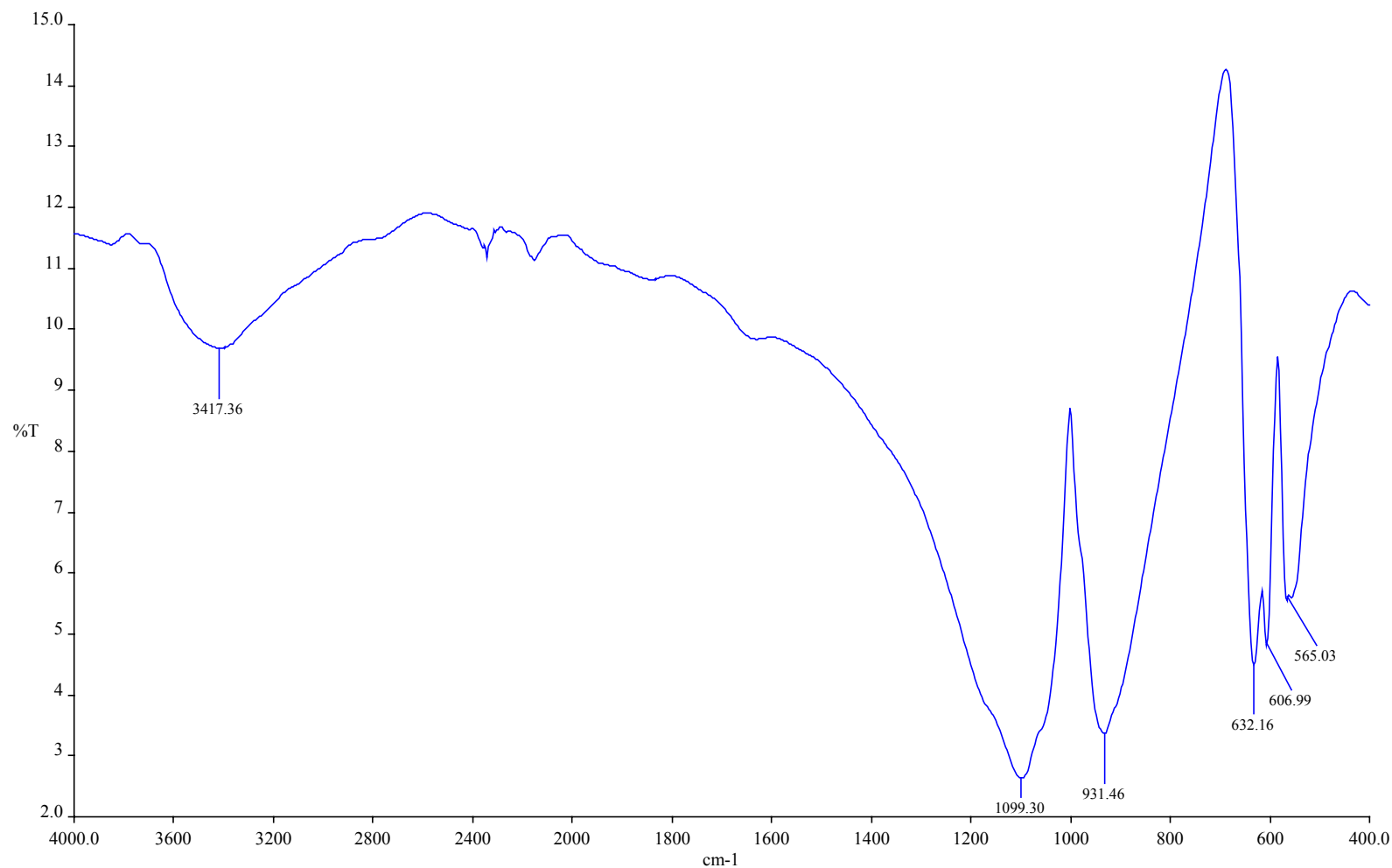


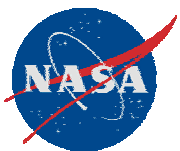
Effect of pressure (void volume) on acid uptake by BN



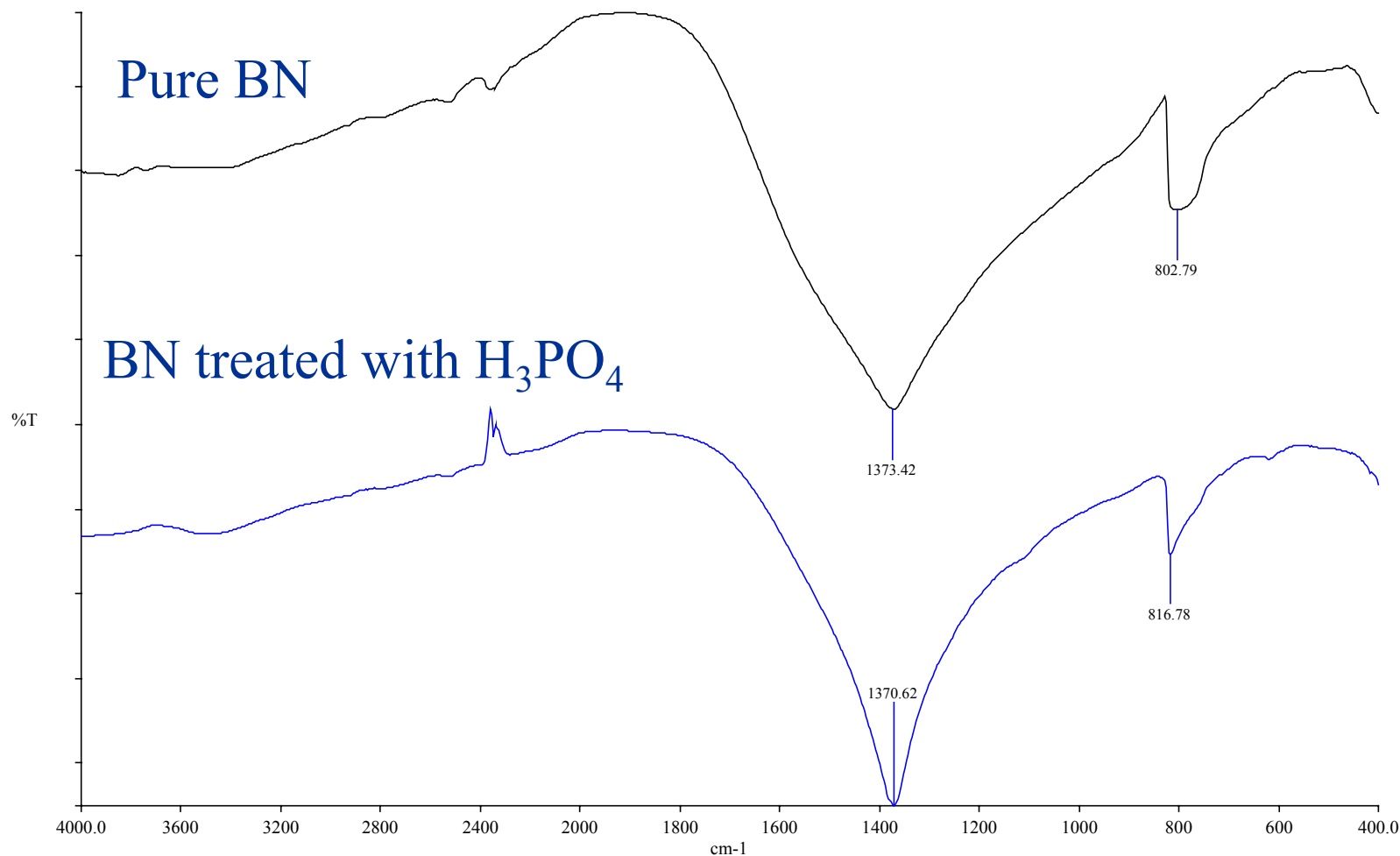


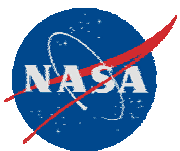
IR spectrum of BPO₄



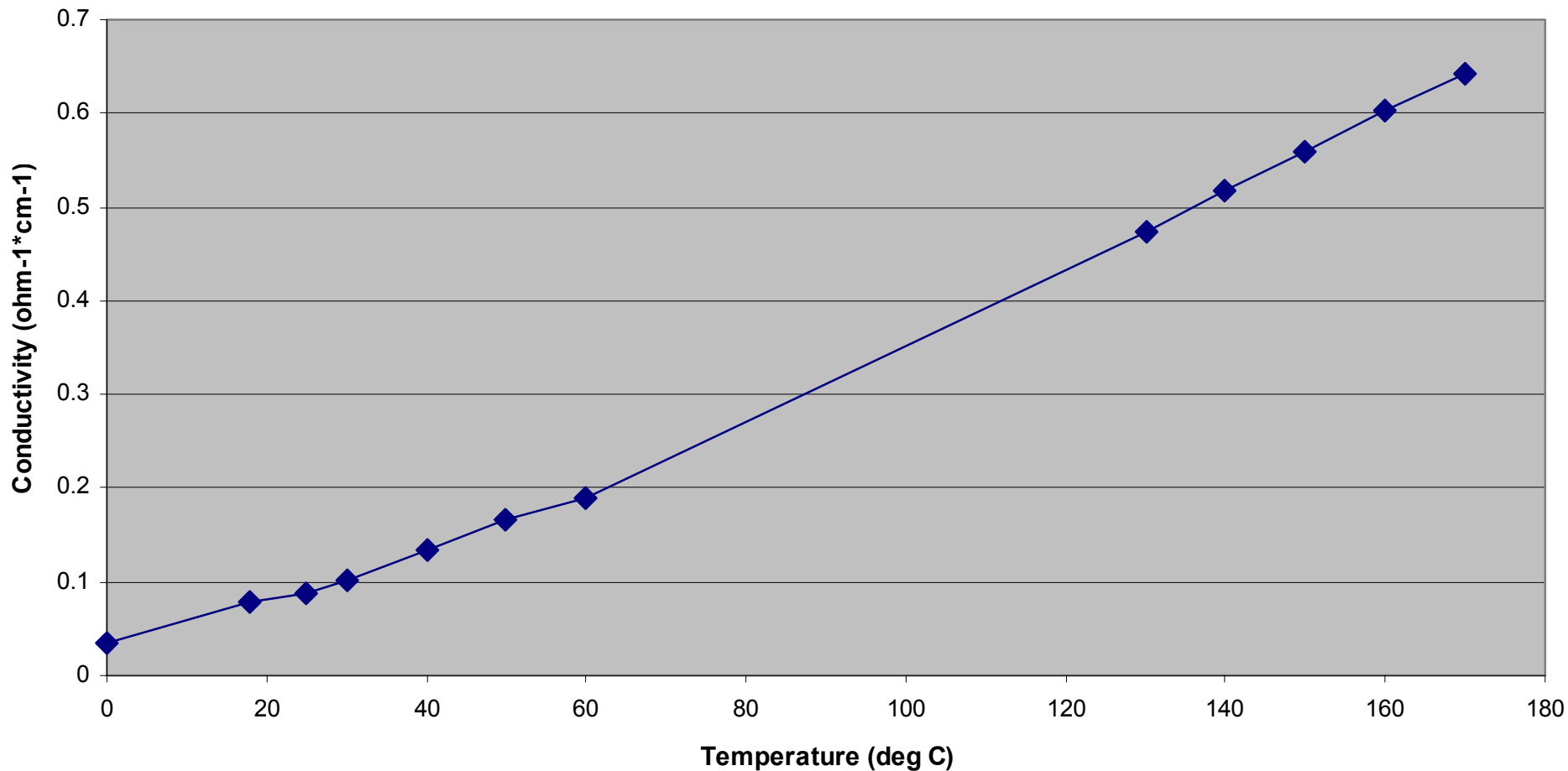


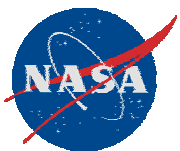
IR spectrum of BN before/after 120 °C H_3PO_4 exposure, rinsing, and drying



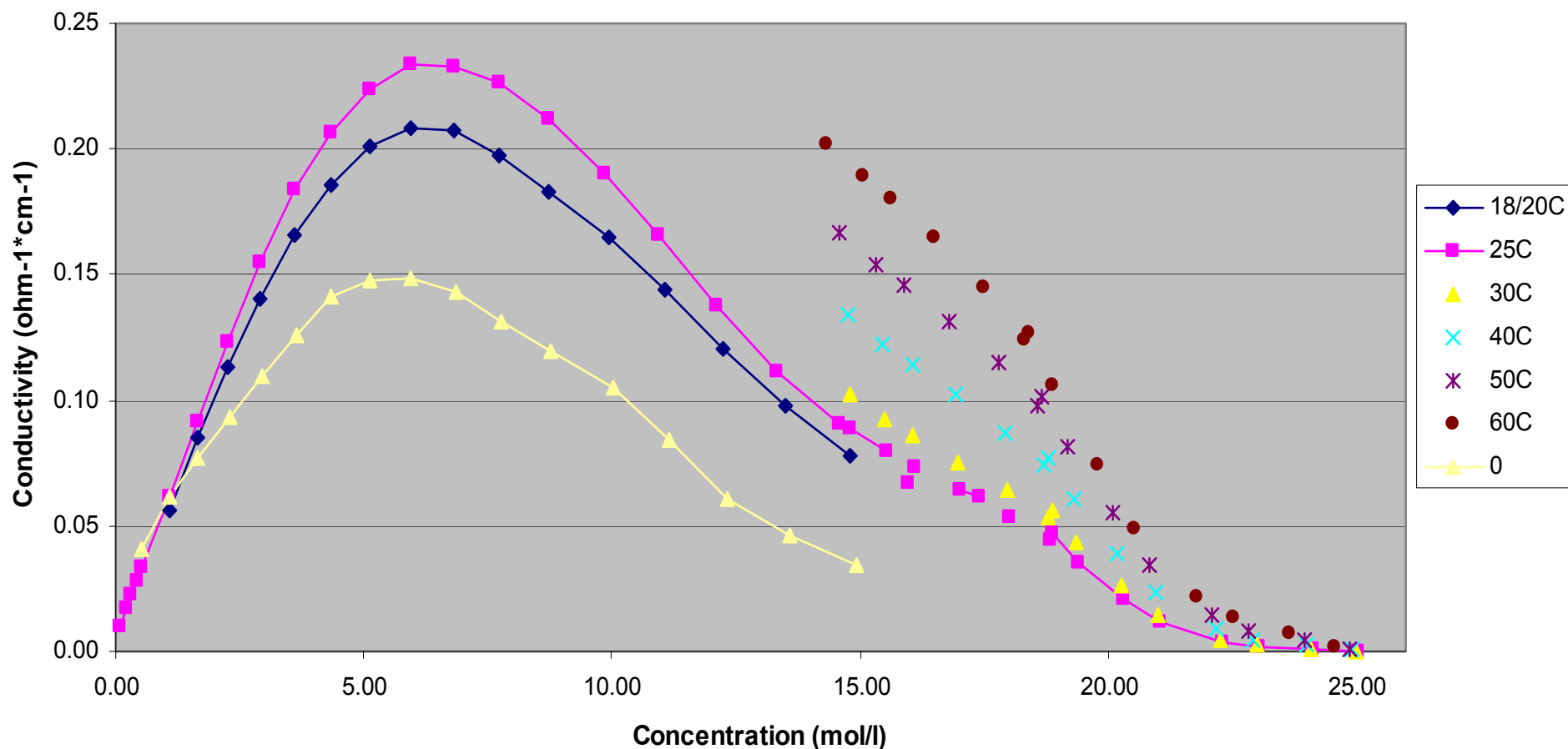


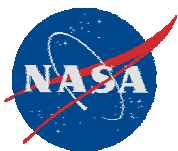
Phosphoric acid conductivity vs T (85% conc)



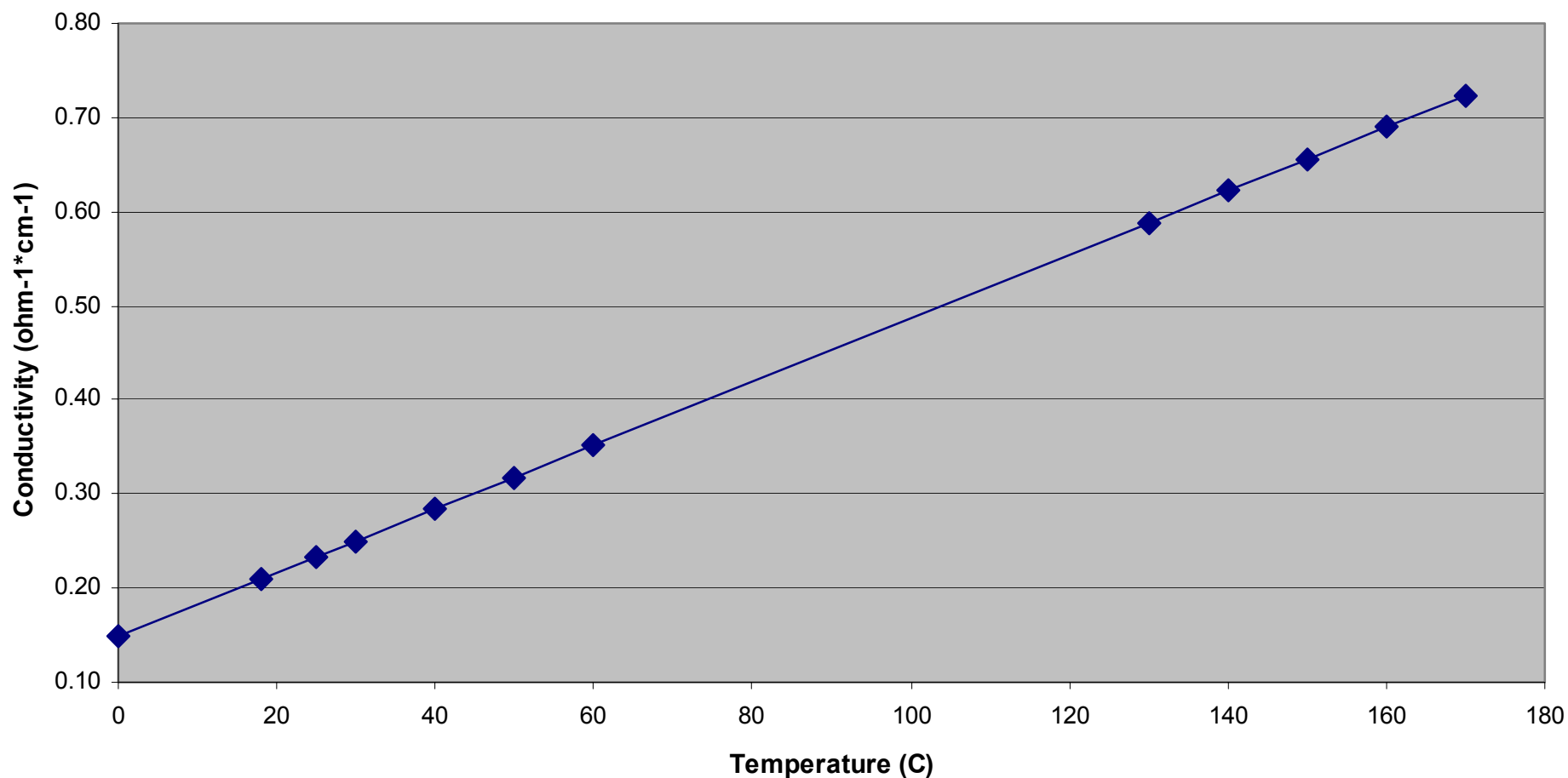


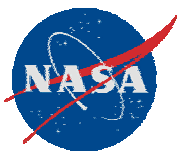
Phosphoric acid conductivity vs concentration at various temperatures



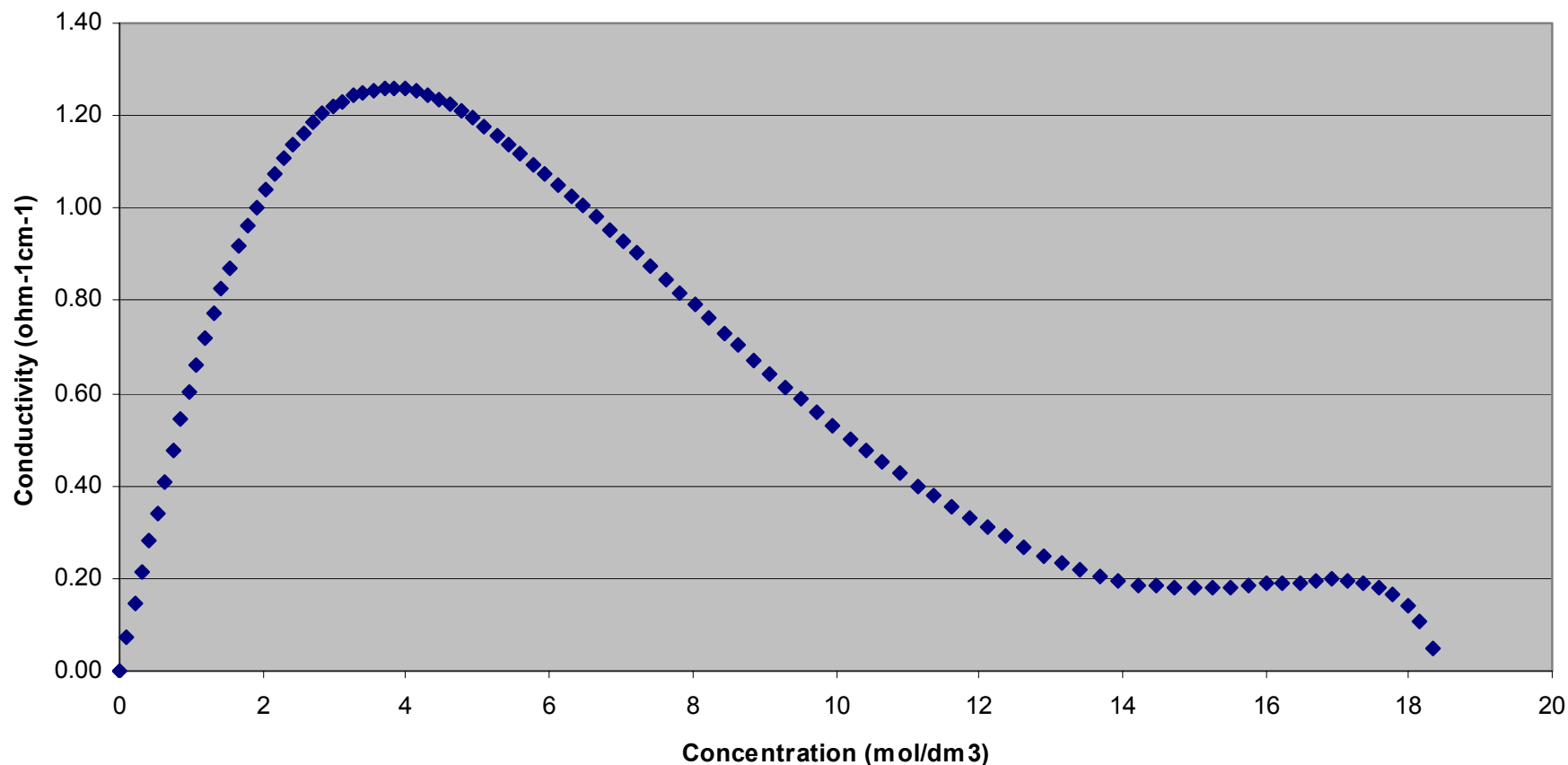


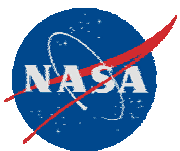
H_3PO_4 conductivity vs T at optimum conc (45%) extrapolated data



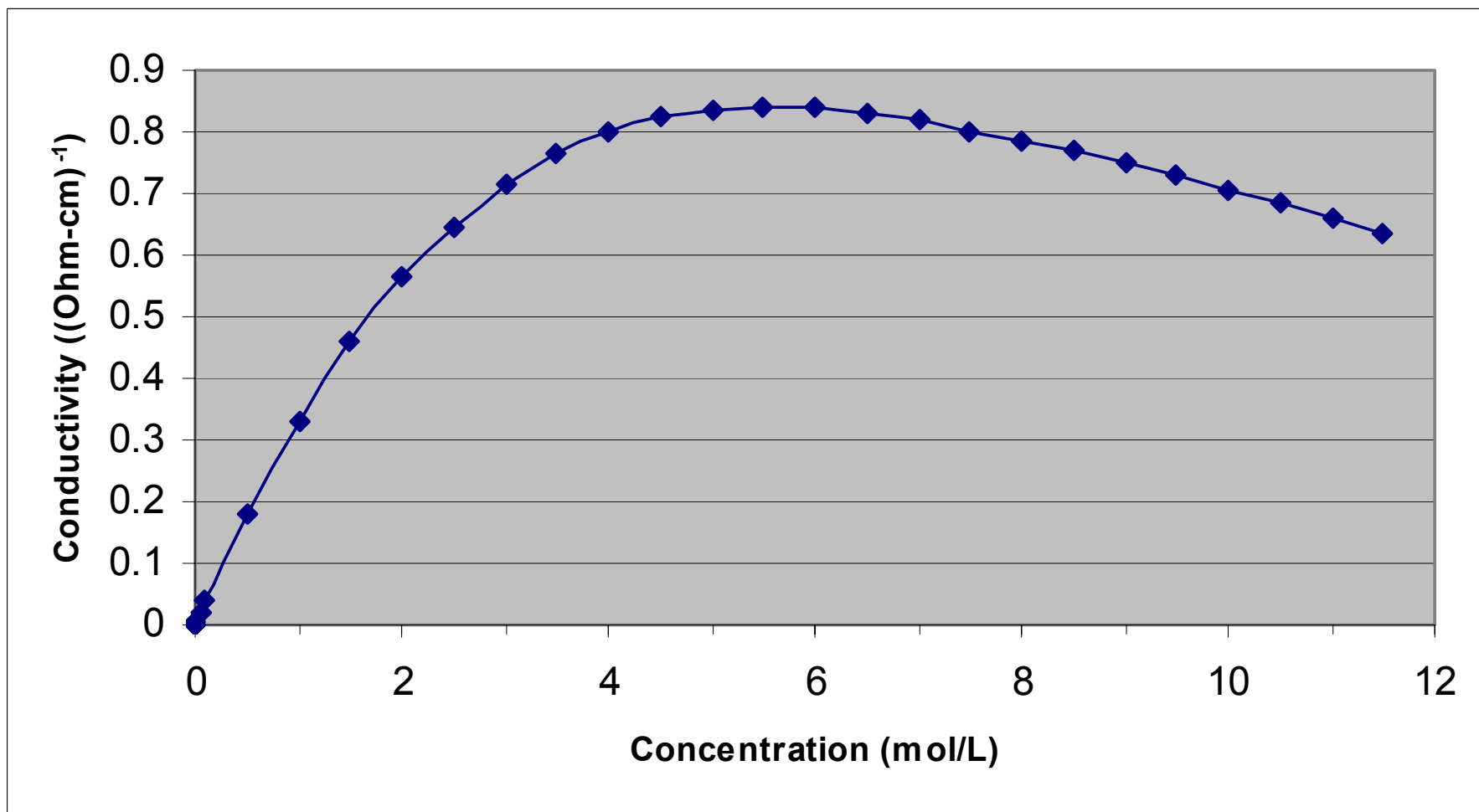


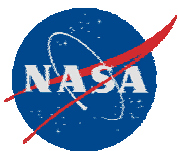
Conductivity vs Concentration for H_2SO_4 at 21 °C





Conductivity vs Concentration for HCl (aq) at 25 °C





Future Plans

Include acid/water mixtures as liquid phase components of electrolyte composites to augment proton conductivities.

Substantiate water content vs conductivity relationships

Establish volatility vs temperature characteristic

Effect of dissolved phosphate salts in H_3PO_4

Estimate differential pressure limits of electrolyte composites

Compare results to BC and SiN analogous systems

Examine chemical/thermal stability of polymeric matrices:

- polyketones

- polysulfones

- polyphenylquinoxalines

- polybenzimidazoles, and

- polybenzoxazoles.