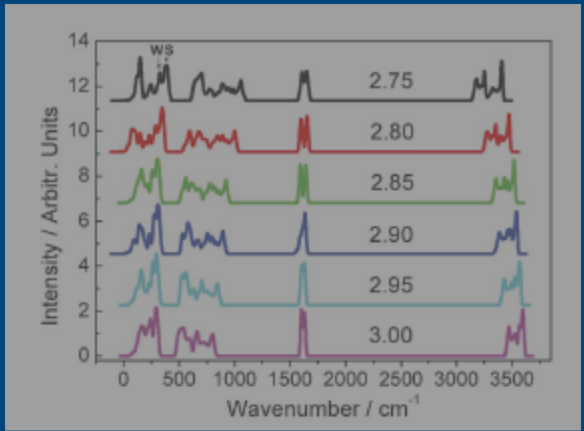
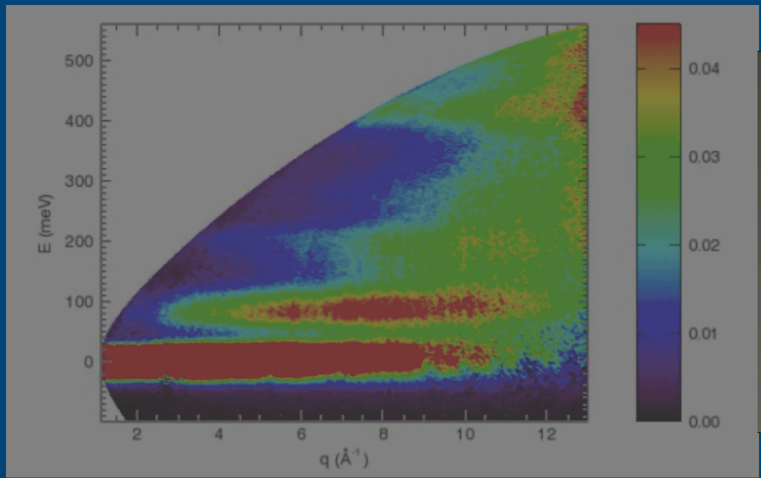
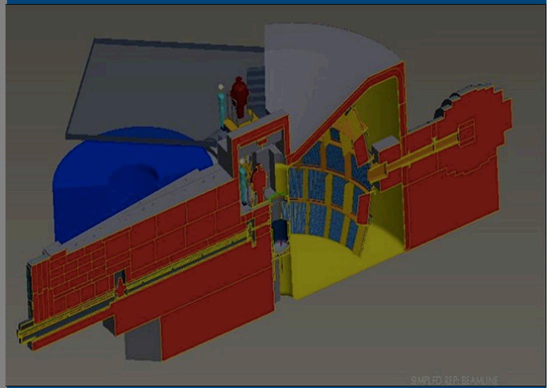
Inelastic neutron scattering from porous anode materials at the Spallation Neutron Source - ORNL







Roberto Senesi

Univ. Roma Tor Vergata, Dip. Fisica and Centro NAST; CNR-IPCF

NAST 2013

Overview

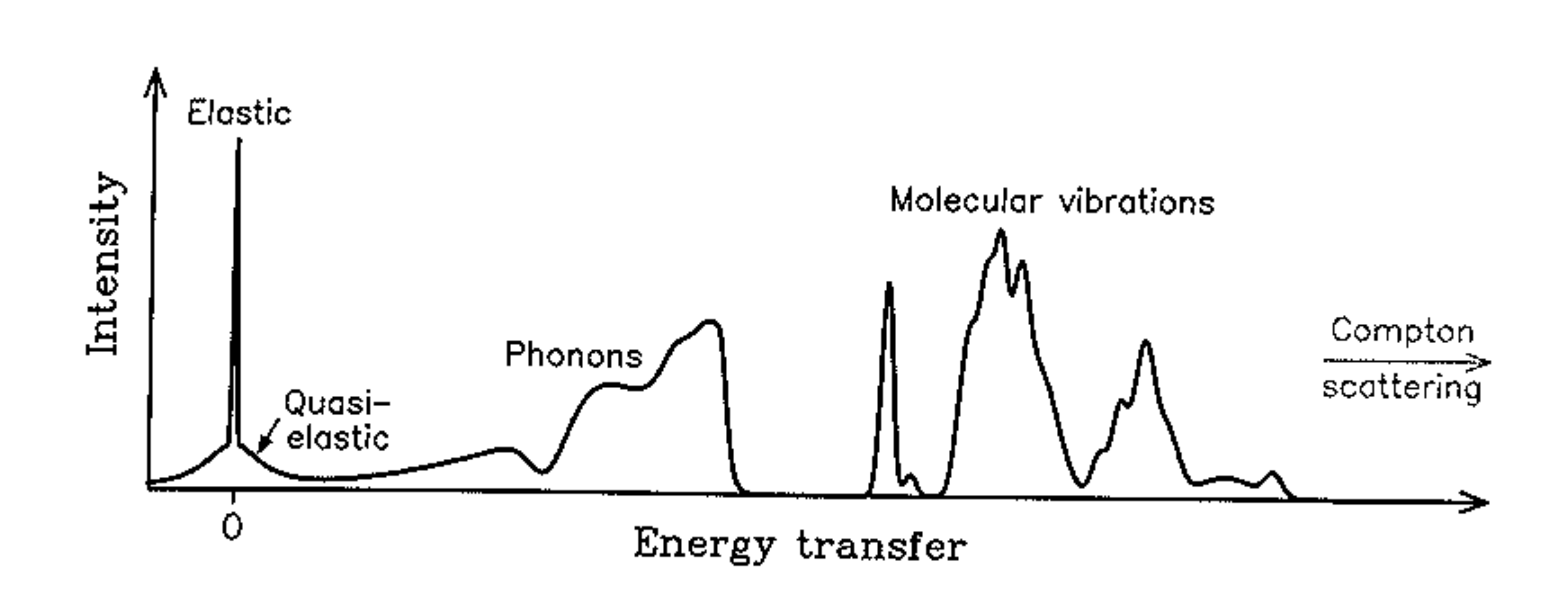
- Inelastic neutron scattering programme within META

•Step 1- probing Vibrational spectra on H-containing systems +proton zero point spectroscopy on H-containing systems

•Step 2- Vibrational spectra, self-diffusion spectra on ionic conducting materials.- preliminary results

Team:C. Andreani, F. Basoli, N. Jalarvo, A. I. Kolesnikov, S. Licoccia, E. Mamontov, E. Perelli Cippo, R. Senesi

Structure determines vibrational energies
But minimized energy determines structure!



From: “Elementary Scattering Theory For X-ray and Neutron Users” D.S. Sivia OUP (2011)

Collective and single-particle excitations-vibrations

Ok! does this help in understanding and improving Ionic conducting materials?

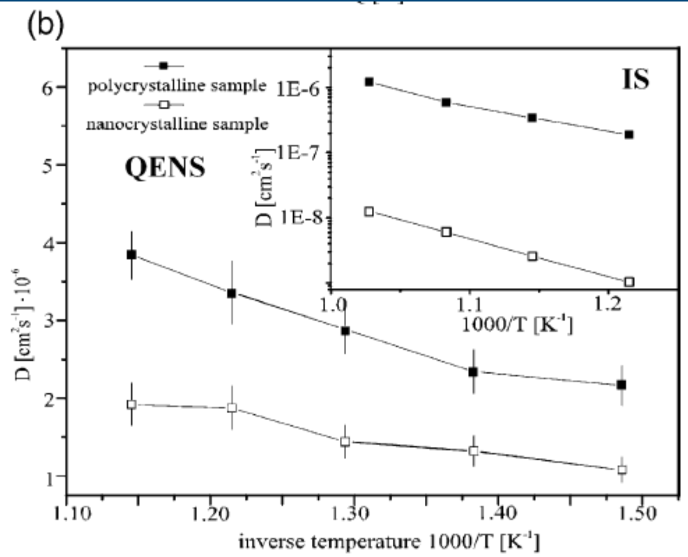


Fig. 5. (a) EISF for nanocrystalline and polycrystalline $BaZr_{0.85}Y_{0.15}O_{2.925}/0.0375H_2O$. The solid line represents the model-dependent fit according to the dumbbell model. (b) Temperature dependence of the diffusive constant of both explored samples in comparison with the results of the impedance spectroscopy (IS).

- Discriminate between effective (conductivity) diffusion and microscopic (chemical) diffusion
- *B. Groß et al.Solid State Ionics 145 (2001) 325–331*

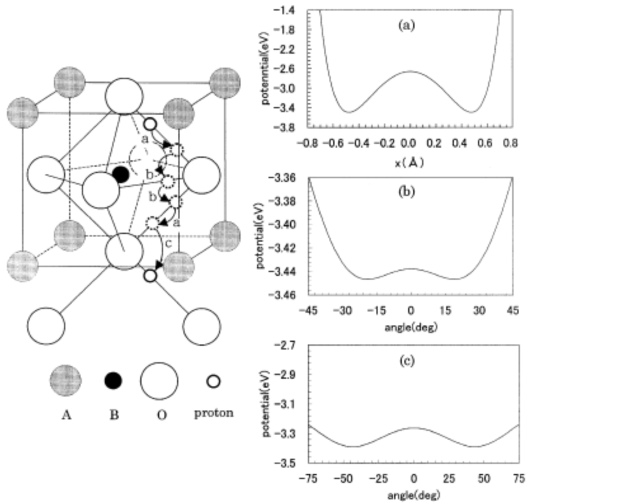
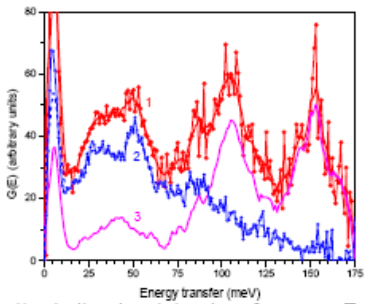


Fig. 1. An example of proton hopping processes in the perovskite structure. An optimum path is shown for the combination of three types of process; (a), (b), (b), (a), (c). Each potential curve for the processes (a), (b) and (c) is depicted for R_{O-O} = 2.9 Å, respectively, in the right side. In (b), two potential minima are sited at about ±30°, and in (c) at just ±45°.

Tunneling mechanism on proton conduction in perovskite oxides,
E. Matsushita Solid State Ionics 145 (2001) 445–450



Proton Incorporation Through Vibrational spectra
Li, Kolesnikov et al, MRS 2004

Figure 4. Generalized vibrational density of states at T=10 K for dry (curve 2) and wet (curve 1) BCZY samples measured on HRMECS with incident neutron energy E_i=200 meV. Curve 3 shows the difference spectrum between the wet and dry samples.

Ok! does this help in understanding and improving Ionic conducting materials?

- Water is of course involved…

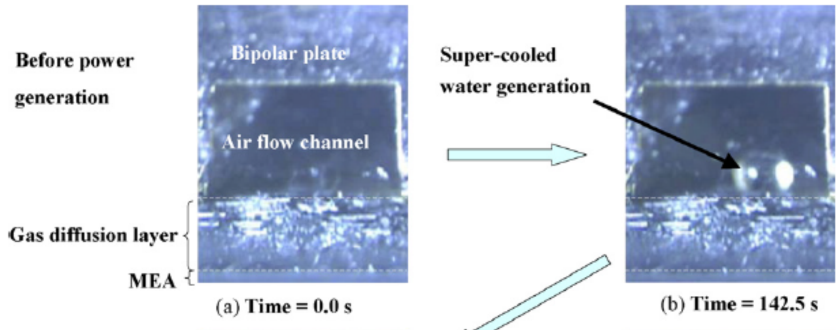
Journal of Power Sources 179 (2008) 547–552

www.elsevier.com/locat

Short communication

Super-cooled water behavior inside polymer electrolyte fuel cell cross-section below freezing temperature

Y. Ishikawa [a,*], H. Hamada [b], M. Uehara [c], M. Shiozawa [a]



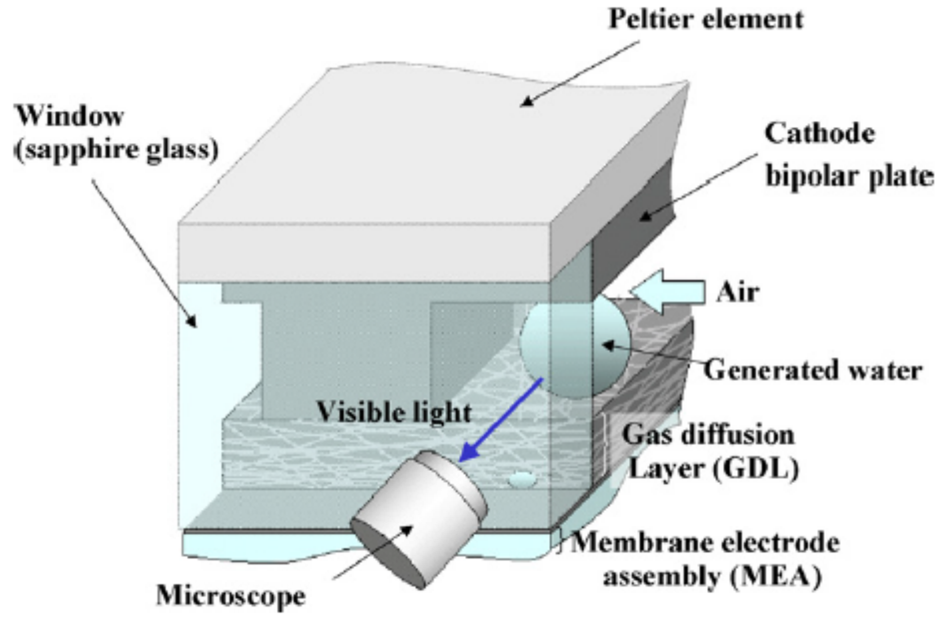


Fig. 1. Schematic image of system for visualizing inside PEFC cross-section.

Training+collaboration

1 Scheme for proposals at large scale facilities
  a) proposals submitted in 2012 accpted and scheduled in Feb 2013

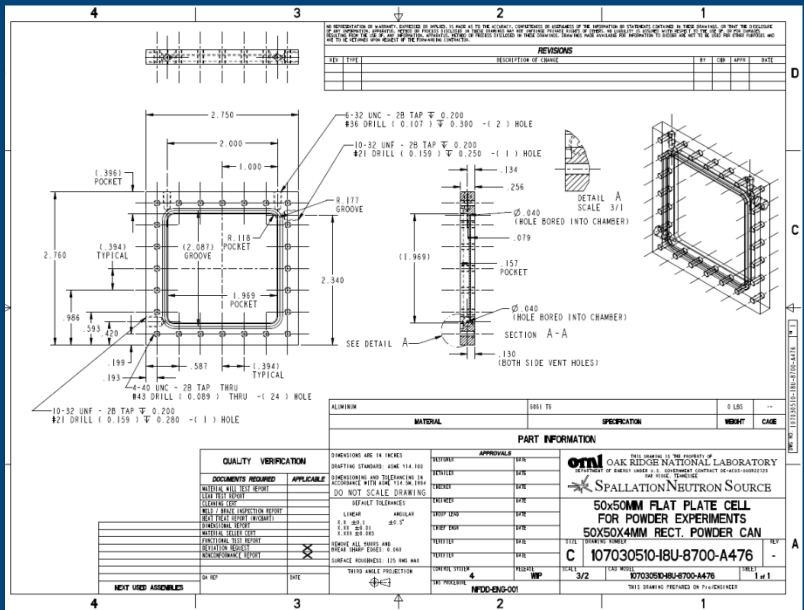
2 Contact with instrument scientists/sample environment (thanks F. Basoli…)

3 Secondments in Aug-Sept. 2012 and Feb 2013
  Basoli, Perelli Cippo

Training+collaboration

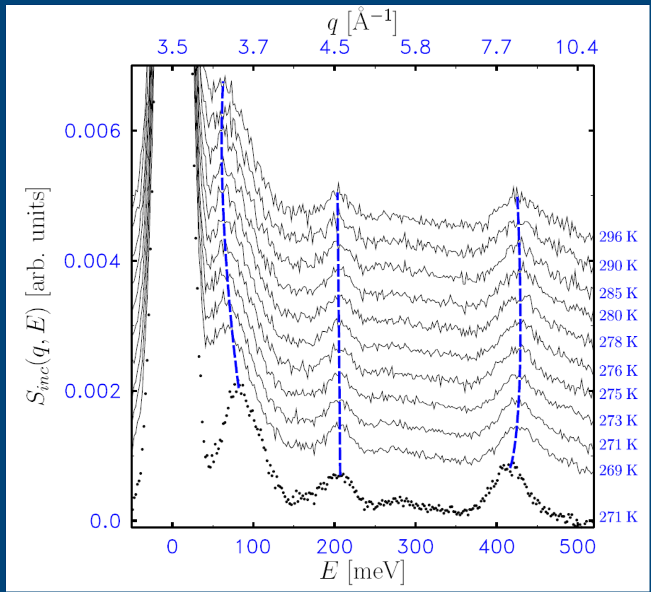
Very good interaction with SNS instrument scientists/ sample Environment

N. Jalarvo, A. I. Kolesnikov, E. Mamontov

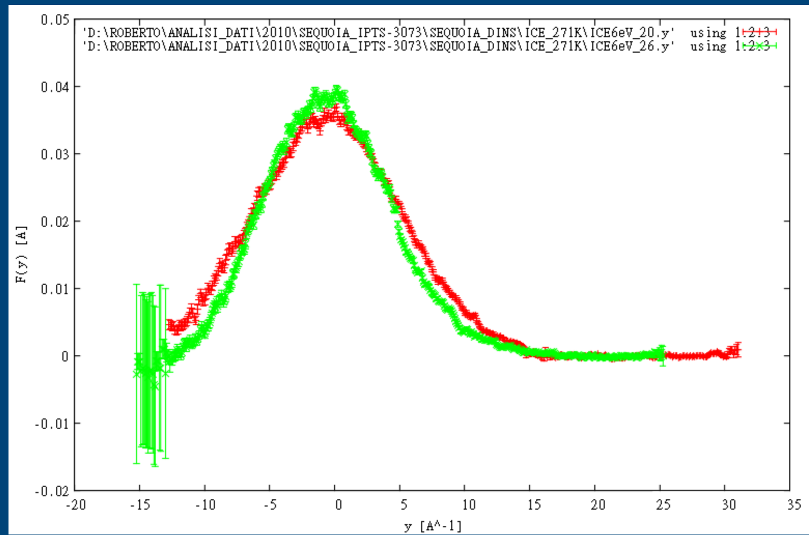


Example: sample container design+
Machining at ORNL; coating in Italy

Deliverables: INS+DINS measurements
Simultaneous measurements possible? YES at SNS- SEQUOIA beamline



INS



DINS=free recoil of protons

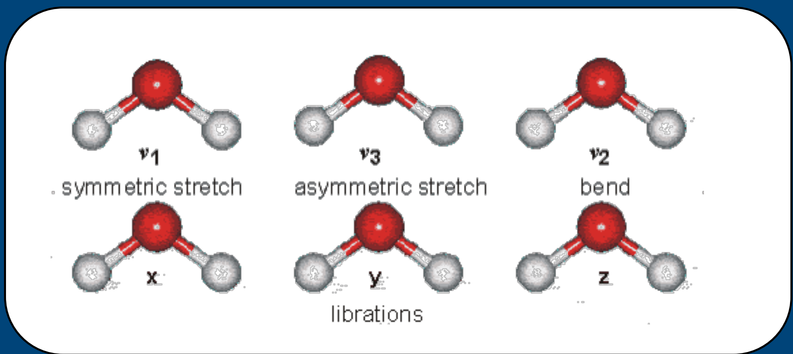
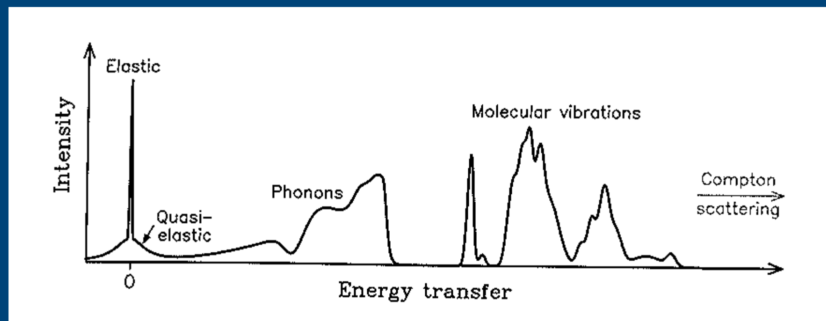
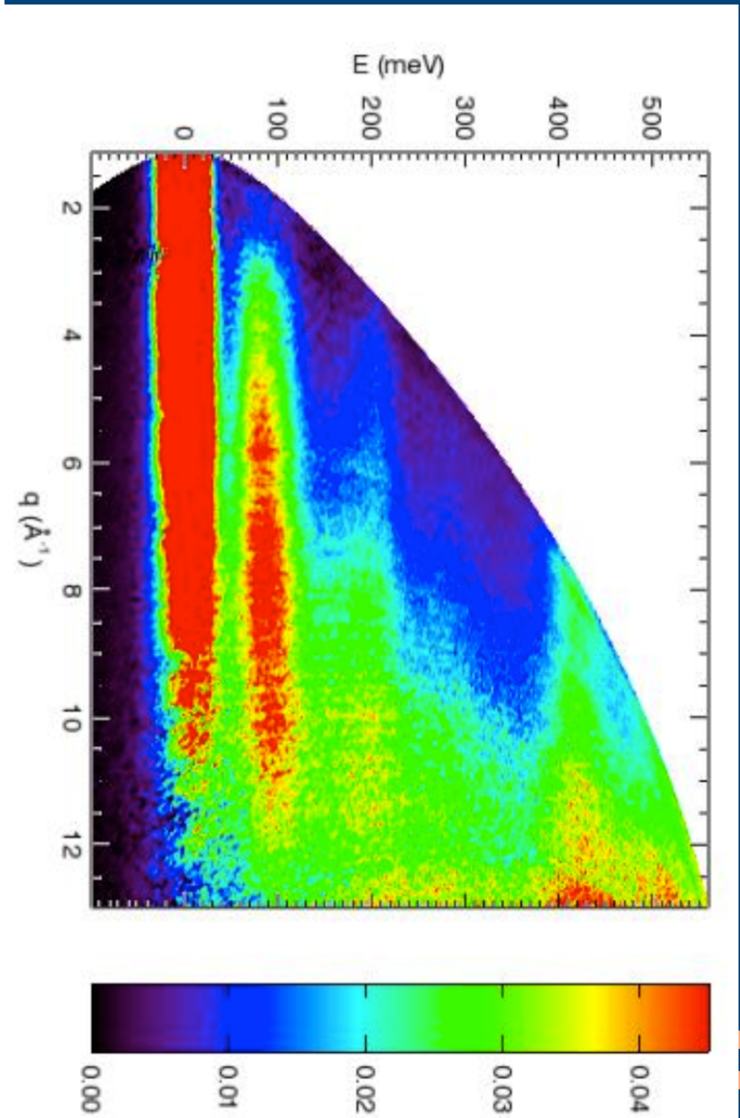
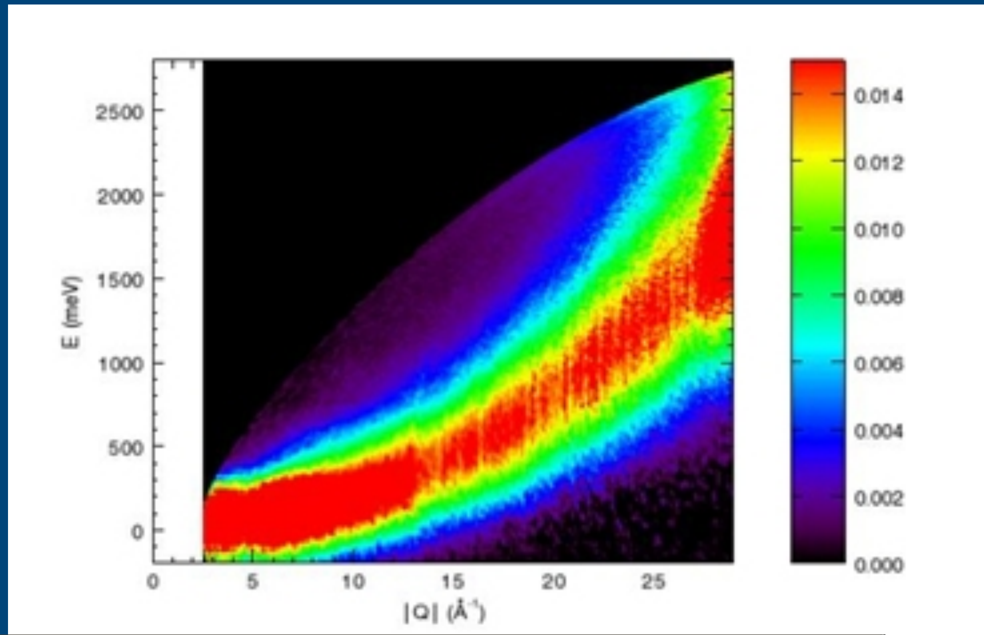


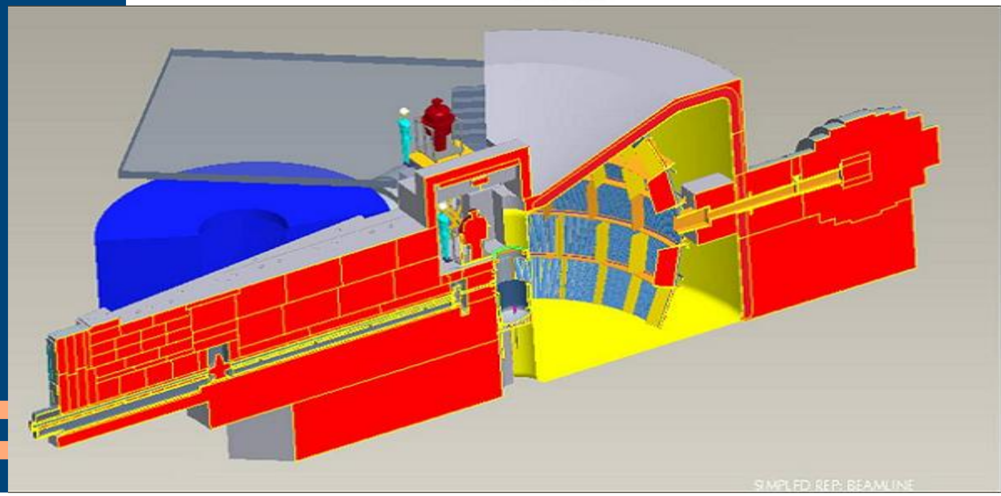
Figure:M. Chaplin, http://www.lsbu.ac.uk/water/index.html



Deliverables: INS+DINS measurements
Simultaneous measurements possible at SNS- SEQUOIA beamline



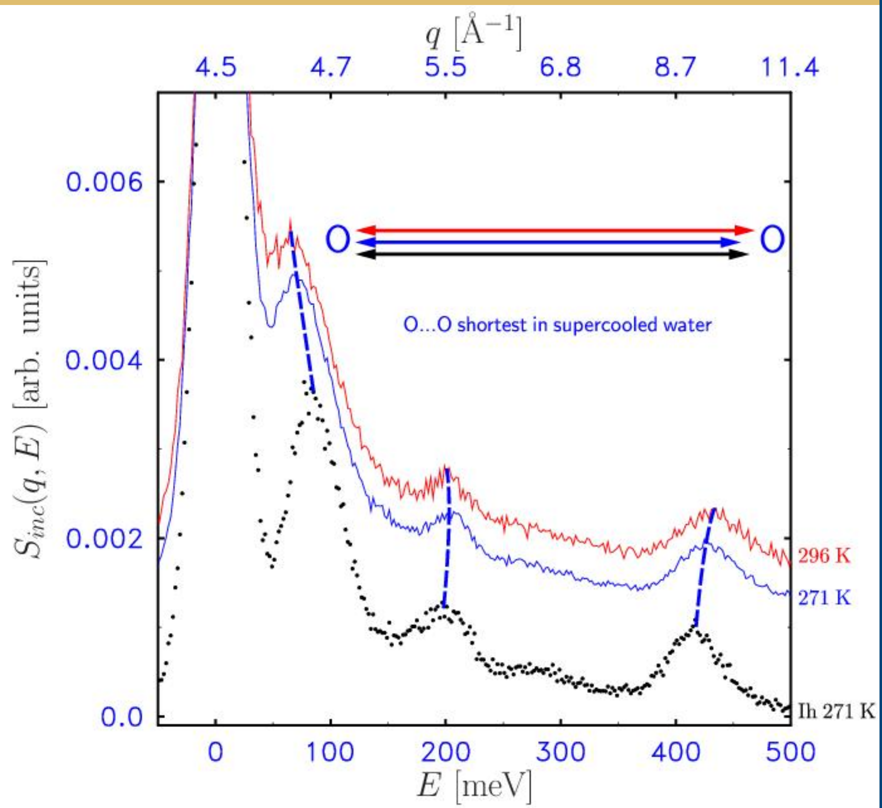


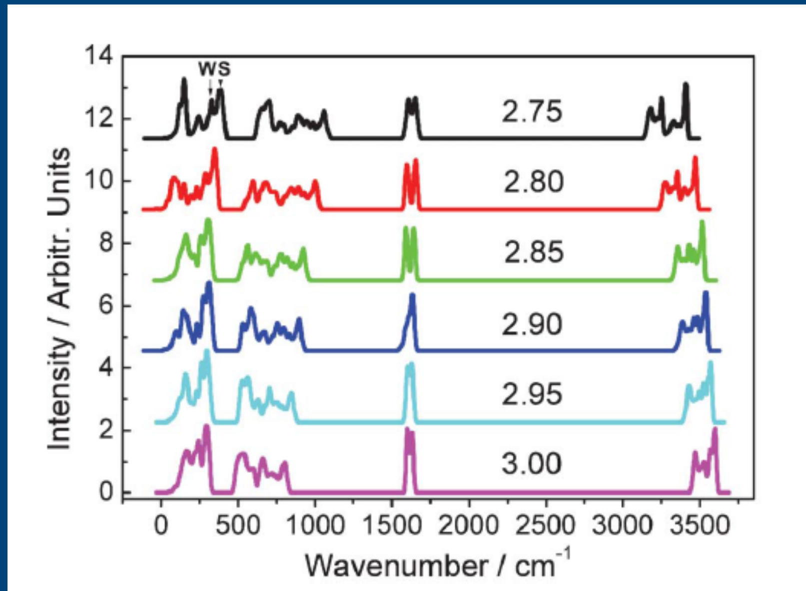


Sensitivity of the technique: First exp on water/ice

Assess the correlations between O…O shortening and red/blue shifts in the vibrational spectrum.

Senesi, Flammini, Murray, Galli, Kolesnikov, Andreani, Submitted (2013)





Zhang et al. RSC Adv 2013- Ice Ic

State	T	Estretch	O…O	(O…O)-(O…O @RT)
GAS	296	460	*	*
S	271	415	2.76	-0.04
L	296	435	2.80	0.0
Supercool	271	425	2.70	-0.1
VHDA	80	424.5	2.70	-0.1

Inelastic Neutron scattering: a probe for H vibrations and Zero Point Kinetic Energy components…

$$lim_{q\to 0}\frac{S_{inc}(q,E)}{q^2}2ME\frac{e^{[2W(q)]}}{[n(E)+1]}=g_{exp}(E)_H$$

For the Stretching range

$$\langle E_K\rangle_{OH}=\frac{3}{4}\int_{355}^{480}g_{exp}(E)_{OH}\,E\,dE$$

Harmonic+decoupling assumption

$$\langle E_K\rangle \approx \langle E_K\rangle_{OHstr}+\langle E_K\rangle_{bend}+\langle E_K\rangle_{libr}$$

Low wave vector+ high energy transfers

$$S(\vec{q},\omega)=\hbar\int d\vec{p}\,n(\vec{p})\,\delta\left(\hbar\omega-\frac{\hbar^2q^2}{2M}-\frac{\vec{p}\cdot\hbar\vec{q}}{M}\right)$$

$$\langle E_K\rangle=\frac{\langle p^2\rangle}{2M}$$

High wave vector+ high energy transfers= Deep Inelastic Neutron Scattering

SAMPLES (F. Basoli)

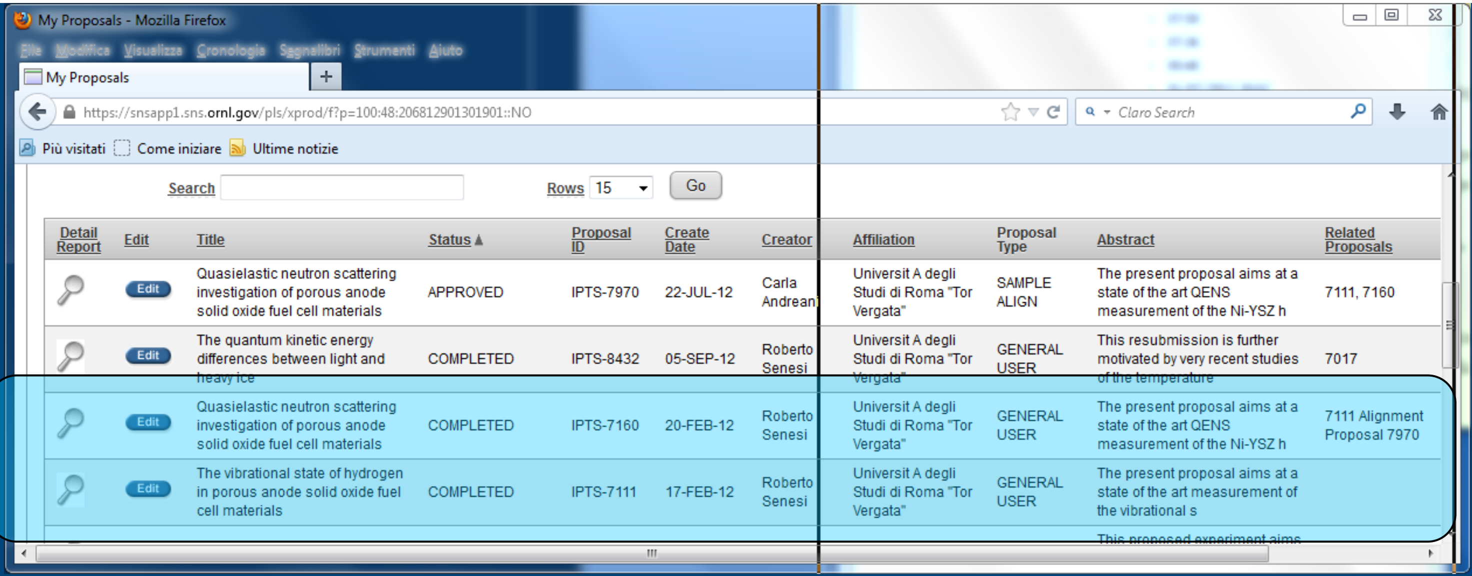
Task 2.1 (Deliverable D2.1)

Yttria Stibilized Zirconia – porous to create a ceramic foam

+ impregnation with $Ni(NO_3)_2 \cdot 6H_2O$

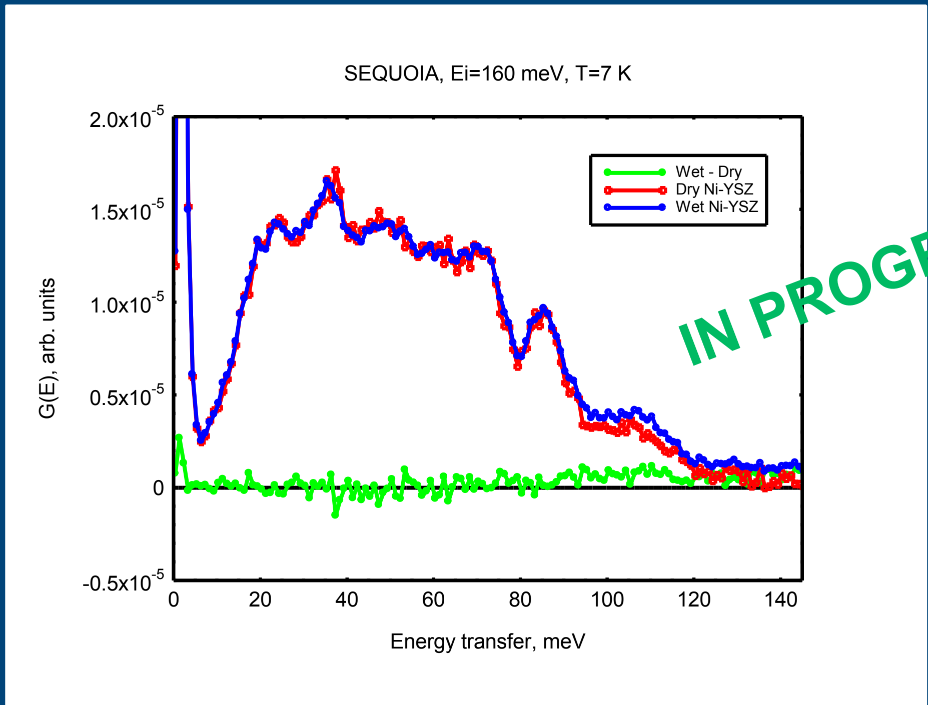
+ treatments to ensure a content of 10% wt of NiO

+hydration in water vapor at 900 C overnight
+then cooled down to 150° C, flowing dry gas to remove bulk water from the pores



My Proposals - Mozilla Firefox

Detail Report	Edit	Title	Status ▲	Proposal ID	Create Date	Creator	Affiliation	Proposal Type	Abstract	Related Proposals
	Edit	Quasielastic neutron scattering investigation of porous anode solid oxide fuel cell materials	APPROVED	IPTS-7970	22-JUL-12	Carla Andreani	Universit A degli Studi di Roma "Tor Vergata"	SAMPLE ALIGN	The present proposal aims at a state of the art QENS measurement of the Ni-YSZ h	7111, 7160
	Edit	The quantum kinetic energy differences between light and heavy ice	COMPLETED	IPTS-8432	05-SEP-12	Roberto Senesi	Universit A degli Studi di Roma "Tor Vergata"	GENERAL USER	This resubmission is further motivated by very recent studies of the temperature	7017
	Edit	Quasielastic neutron scattering investigation of porous anode solid oxide fuel cell materials	COMPLETED	IPTS-7160	20-FEB-12	Roberto Senesi	Universit A degli Studi di Roma "Tor Vergata"	GENERAL USER	The present proposal aims at a state of the art QENS measurement of the Ni-YSZ h	7111 Alignment Proposal 7970
	Edit	The vibrational state of hydrogen in porous anode solid oxide fuel cell materials	COMPLETED	IPTS-7111	17-FEB-12	Roberto Senesi	Universit A degli Studi di Roma "Tor Vergata"	GENERAL USER	The present proposal aims at a state of the art measurement of the vibrational s	



IN PROGRESS