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A new apparatus design for high temperature (up to 950 °C) quasi-elastic neutron scattering in a controlled gaseous environment

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A design for a sample cell system suitable for high temperature Quasi-Elastic Neutron Scattering (QENS) experiments is presented. The apparatus was developed at the Spallation Neutron Source in Oak Ridge National Lab where it is currently in use. The design provides a special sample cell environment under controlled humid or dry gas flow over a wide range of temperature up to 950 °C. Using such a cell, chemical, dynamical, and physical changes can be studied *in situ* under various operating conditions. While the cell combined with portable automated gas environment system is especially useful for *in situ* studies of microscopic dynamics under operational conditions that are similar to those of solid oxide fuel cells, it can additionally be used to study a wide variety of materials, such as high temperature proton conductors. The cell can also be used in many different neutron experiments when a suitable sample holder material is selected. The sample cell system has recently been used to reveal fast dynamic processes in quasi-elastic neutron scattering experiments, which standard probes (such as electrochemical impedance spectroscopy) could not detect. In this work, we outline the design of the sample cell system and present results demonstrating its abilities in high temperature QENS experiments. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4929580>]

I. INTRODUCTION

As a class of materials, proton conductors are employed across a diverse range of technological applications such as batteries,¹ fluorescent lamps,^{2,3} hydrogen separation membranes, hydrogen and humidity sensors,⁴ and proton conductor electrolytes for solid fuel cells.^{5,6} One of the most important applications of this material class is high-efficiency electrochemical energy conversion and storage. Proton conduction fuel cells could be transformative power sources for transportation across a broad range of vehicles from automobiles to super-stealth vessel submarines.⁷ These fuel cells have distinctive favorable features; they are highly efficient, environmentally friendly, and silent.⁸

This study focuses on the design of an apparatus with a sample cell environment used in conjunction with neutron instrumentation, such as the Backscattering Silicon Spectrometer (BASIS), to help understand dynamics and diffusive behavior of protons in the phosphate family's rare-earth members, which are solid electrolyte candidates for proton-conducting solid oxide fuel cells (SOFC).⁹ Our system along with BASIS is capable of being used to study the dynamics of many different materials such as oxides, battery materials, and other proton conducting materials, such as lanthanum tungstate¹⁰ and yttrium-doped barium zirconate.¹¹

The impact of aliovalent (Sr, Ca, Ba) doping on proton conductor materials, such as lanthanum orthophosphate (LaPO₄), and on metaphosphate (LaP₃O₉) materials has been investigated experimentally in a number of macroscopic scale studies, mostly using Electrochemical Impedance Spectroscopy (EIS).^{12–14}

A less commonly used but powerful technique is Quasi-Elastic Neutron Scattering (QENS), which probes single particle dynamics with a particularly high sensitivity to the motion of protons.^{9,15–24} The sample cell and associated equipment were operated at the neutron beam at BASIS at the Spallation Neutron Source (SNS) in Oak Ridge National Laboratory (ORNL). BASIS can probe dynamic motions in different systems on the pico- to nanosecond time scale and on the length scales from ~3 to 31 Å. QENS signal at BASIS can be measured at a wide momentum-transfer range of 0.2 Å⁻¹ < Q < 2 Å⁻¹ and energy transfers (ω) of up to ±200 μeV with 3.5 μeV resolution.

Currently available sample environments allow for temperature investigations below 500 K, limiting the use of QENS as a probe in studying high temperature proton conductors. This limitation arises from two factors: (1) the type of material used for the sample holder and container and (2) the dehydration of the samples at elevated temperatures during the experiment. In previously reported QENS studies, the samples were

charged with protons prior to the QENS experiment and to maintain the sample hydration during the QENS experiment; the sample was tightly sealed inside a can. Most of the time, the can was aluminum^{15–18} and sometimes the aluminum can was coated with platinum to prevent corrosion.¹⁸ The current article proposes a new sample environment built and used in SNS at ORNL to study the dynamics of diffusion in proton conductors that operate at high temperatures. The sample cell system (SCS) inside the furnace allows for measuring at temperatures up to 950 °C and maintains sample hydration at elevated temperatures through the QENS experiment. This system can switch between humid and dry environments during the QENS experiment and also facilitates the flow of various gases.

II. DESIGN CONSTRAINTS

A. Safety considerations

The apparatus design at neutron facilities coupled with the safety standards and safety regulations aims to maximize the safety of the instrumentation for the users, the instrument scientists, the environment, and the neutron facilities. The main concern in that regard is radiation. In order to minimize radiation from the sample cell system, a material is used that has low neutron capture cross section, such as fused quartz (SiO_2), Al, Pt, or Nb.

The calculated radiation dose equivalent rates for Pt, Al, and Nb cans at a distance of 2.5 cm (nominally, the distance of a detector active area from the can) are 0.01 mSv/h, ~0 mSv/h, and 0.6 $\mu\text{Sv/h}$, respectively, after being placed in the neutron beam for 2 days. From an initial value of 0.01 mSv/h, it would have taken approximately 4 days for the Pt can dose equivalent rate to have fallen below 0.002 mSv/h. A 0.02 mSv/h value measured at 30 cm ensures that the area in which the scientist is working does not become a Radiation Area.

After the Pt can had been in the neutron beam (the area of which is about 9 cm²) for 2 days, we scanned the radiation activity of the Pt can. The time between stopping the beam and the radiation scan was about 2 h, and measurement on the empty metal container was <0.002 mSv/h contact. The measured normal background dose rate is 0.2 $\mu\text{Sv/h}$ using a sensitive field detector (like a Bicron Microrem meter).

This difference between the measured radiation of the Pt can and the calculated one could be related to some combination of uncertainty in distance measurement, irradiation time, and estimated flux. Although the radiation activities of Al, Nb, and fused quartz after the neutron experiment are undetectable under normal conditions, the Al and Nb cans are not suitable under the current environmental conditions of extreme high temperature (up to 900 °C) and humid atmosphere. Therefore, fused quartz or Pt is better choices in this situation.

B. Risk of tightly sealed cans deforming inside the neutron chamber

In the previous experiments, the sample container (usually aluminum) was sealed tightly to maintain the humidity level and keep protons inside the sample at elevated temperatures.

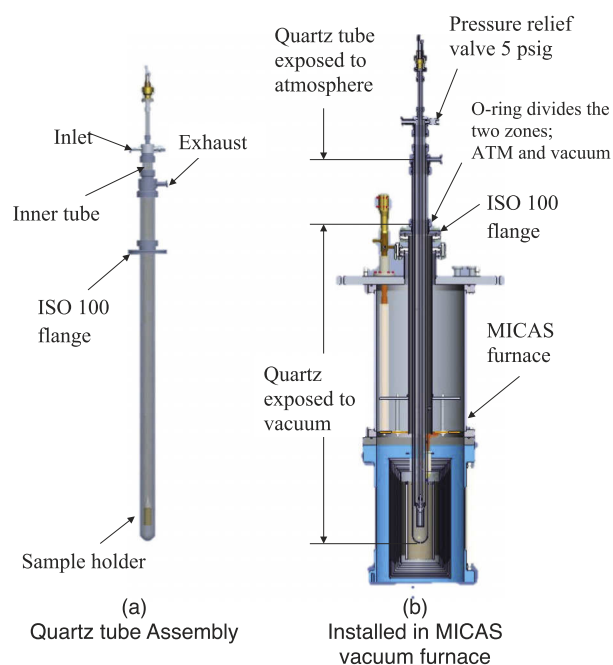


FIG. 1. (a) The fused quartz tube of the SCS. The Pt sample holder connected by inner fused quartz tube and surrounded by outer fused quartz tube. (b) The sample cell system installed in MICAS vacuum furnace at SNS sample environment.

However, water pressure inside the sealed can increases as a function of temperature, and if the sample has enough water, the can could break or deform inside the neutron chamber resulting in leakage. To remedy these problems, the newly designed apparatus is equipped with a mass flow controller (MFC). The constant flow of humid gas maintains the protons inside the sample at elevated temperatures during the QENS experiment. The open can, located inside of a fused quartz tube, limits water vapor pressure buildup, ensuring safety during experiments. That fused quartz tube has an inlet and an exhaust opening as shown in Figures 1 and 2. The pressure relief is used to prevent the quartz tube from overpressure in the event that the output port was to become blocked for any reason.

C. Candidate materials for instrumentation

Aluminum (Al), niobium (Nb), and fused quartz (SiO_2 GE TYPE 214) are considered the norm when it comes to materials used for sample cans in QENS experiments. They have very low incoherent scattering cross sections and absorb neutrons very weakly from the beam (low radiation activation), as quoted in Table I. Pure Al has a relatively low melting point 660 °C, compared to other elements such as Nb and Pt whose melting points are 2477 °C and 1760 °C, respectively. Al works very well for QENS experiments at temperatures below 500 °C. Unfortunately, for higher temperatures, thermal stress makes Al susceptible to distortions. For high temperature QENS experiments under humid atmospheres, niobium is not a good choice, as Figure 3 shows. Niobium's corrosion resistance falls with increasing temperature in humid atmosphere. In contact with water vapor, niobium reacts strongly with oxygen and with hydrogen. Hydrogen can easily

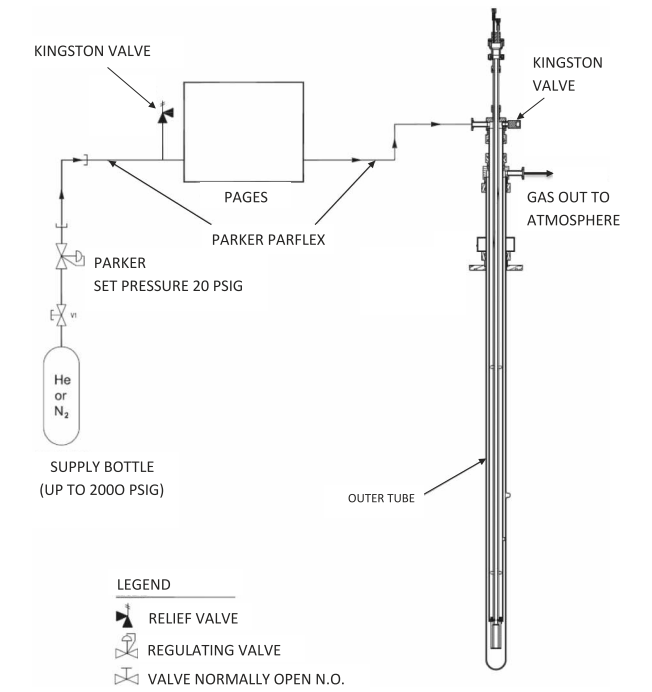


FIG. 2. Sample cell system connected to PAGES. PAGES system is designed to deliver gas to the sample cell via three separate gas channels.

dissolve and migrate within niobium, reducing its ductility and transforming niobium to a brittle material vulnerable to failure. In addition, at high temperatures, niobium may react with construction parts that contain oxides. **Platinum (Pt)**, by contrast, is a very unreactive metal and is chemically and mechanically stable. It is very resistant to corrosion, even at high temperatures. In a neutron beam, Pt has a relatively low incoherent scattering cross section as well as a low absorption cross section compared to other elements presented in the table such as Cd and Ag. Further, compared to gold, silver, and copper, platinum is more ductile. Platinum routinely appears as an electrocatalyst in fuel cells.²⁶ Porous Pt electrodes are used for AC impedance measurements.^{9,27} Compared to Al, Nb, and SiO₂, Pt has a higher neutron absorption cross section. A sample holder made of platinum is ideally suited to study the dynamics of proton conductor electrolytes. The inner and outer wall thickness of the Pt can is 0.025 cm which must

TABLE I. The following are neutron cross section values in barn for some relevant materials.²⁵ where σ_{coh} , σ_{inc} , σ_{scatt} , and σ_{abs} are the coherent, incoherent, scattering, and absorption cross sections, respectively. The last column shows the melting point in °C, where applicable.

Material	σ_{coh}	σ_{inc}	σ_{scatt}	σ_{abs}	Melting point
H	1.757	80.260	82.020	0.333	N/A
SiO ₂	10.627	0.004	10.631	0.171	1683 ^a
Pt	11.58	0.13	11.71	10.300	1760
Nb	6.253	0.002	6.255	1.15	2477
Al	1.495	0.008	1.503	0.231	660
Cu	7.465	0.550	8.030	3.780	1085
Ag	4.407	0.580	4.990	63.300	961.8
Au	7.320	0.430	7.750	98.650	1064
Cd	3.040	3.460	6.500	2520.000	321.1

^aThere is no melting point for fused quartz, this is the softening point instead.



FIG. 3. Niobium embrittled by water at elevated temperature.

be traversed four times for the transmitted beam. For normal incidence (the center of the beam), the calculated transmission of the sample cell is 0.79.

As for fused quartz, its macromolecular structure and very strong Si–O bond make it very stable chemically. It does not react with many materials, even at relatively high temperatures. Due to these characteristics, many neutron facilities use it to design and build tubes and sample cells.²⁸ The flexibility of the apparatus design presented here enables the user to switch cans easily and with little effort in a way that suits the purpose and restrictions of the experiment.

III. APPARATUS DESIGN FOR HIGH TEMPERATURE QUASI-ELASTIC NEUTRON SCATTERING

Figures 1 and 2 show the sample cell systems created to study the proton conductor material using quasi-elastic neutron scattering under different atmospheres. The fabricated apparatus for the SCS was designed in accordance with good vacuum practice. The contaminants that result from the fabrication and machining processes (in the form of dirt, grease, and oil) were removed using suitable solvents such as de-ionized water. Helium leak tests were performed on the setup, and the fused quartz tube insert was assembled into the Micas vacuum furnace. The sample cell setup showed no detectable leak greater than 10^{−7} Torr l/s using a Mass Spectrometer Leak

Detector (MSLD). In addition, the parts were inspected using visual, dimensional, and liquid penetrant methods.

All of the valves and flanges were made from stainless steel, whereas the O-rings were made of viton; the inner and the outer tubes were made from fused quartz. The outer fused quartz tube is 61 in. long. An inlet allows the gas to flow through the inner tube and to the sample. The gas exits between the inner and outer tubes. To prevent overpressure, a Kingston pressure relief valve is attached to the tube assembly. The O-ring and an ISO 100 flange divide the two zones: the ATM and the vacuum environment. The MICAS furnace and 48 in. of the fused quartz tube are exposed to the vacuum. Heat is transferred from the MICAS furnace to the fused quartz tube by radiation. The sample inside the fused quartz tube is held in a helium exchange-gas chamber. The wet/dry He gas enters the inner fused quartz tube through the inlet and is delivered to the sample inside the Pt sample holder. Heat is transferred from the fused quartz tube to the sample by convection and radiation. The heating process is very rapid; in a few hours, the sample's temperature can reach up to 950 °C. This system is very suitable for a sample which is hydrated/dehydrated quickly. For safety reasons, the fused quartz tube's maximum operating temperature is limited to 950 °C. In addition, the outer tube must be replaced after 2 weeks of operation. One disadvantage of the sample cell system is that it can take only one sample at a time. Sample changing requires that the fused quartz tube and fused quartz stick be cooled. The fused quartz sample stick with the sample holder can be pulled from the fused quartz tube, while the inner and outer fused quartz tubes remain in the furnace.

A. Sample holder

The sample transmission factor is wavelength dependent. It also depends on the shape and geometry of the scattering

sample, including the sample holder. To optimize the sample transmission factor, the material was chosen to be as thin as possible, and to obtain an isotropic multiple-scattering distribution,^{29,30} an annular cylinder with a double-walled sample holder was used for the QENS measurements. Placed inside an inner fused quartz tube as shown in Figure 4, the sample holder is connected to the quartz stick by pivotal support and stands perpendicular to the scattering plane defined by the incoming and outflowing neutron beams, which are measured by the BASIS at SNS. For low temperature measurements (<500 °C), the sample holder can be made from aluminum. For high temperature measurements, however, the sample holder can be made from fused quartz or platinum foil 0.025 cm thick as was used for reported QENS measurements. These materials can also be used at relatively low temperatures as well. The sample holder is composed of three main parts: an outer cylinder, a movable inner cylinder, and a pivotal support. The sample's thickness can be controlled by choosing one of two inner cylinders, resulting in sample thickness 0.267 cm or 0.71 cm.

B. Miccas Furnace Generation I

MICAS Furnace Gen I is a radiant heat, vacuum furnace designed and built at the Spallation Neutron Source by the Sample Environment Development and Operations teams. MICAS is designed to operate at temperatures of up to 1600 °C with a set of 8 nested Nb heat shields, a Nb heating element, and a high temperature center stick. After commissioning, the furnace was upgraded to run with a set of 5 nested vanadium heat shields and a vanadium heating element, using the same center stick. The system has a 330 A 20 V DC power supply which allows for a high current, low voltage operation. The heating element surrounds the sample space, and as the current is applied to the element it heats up and radiates heat upon

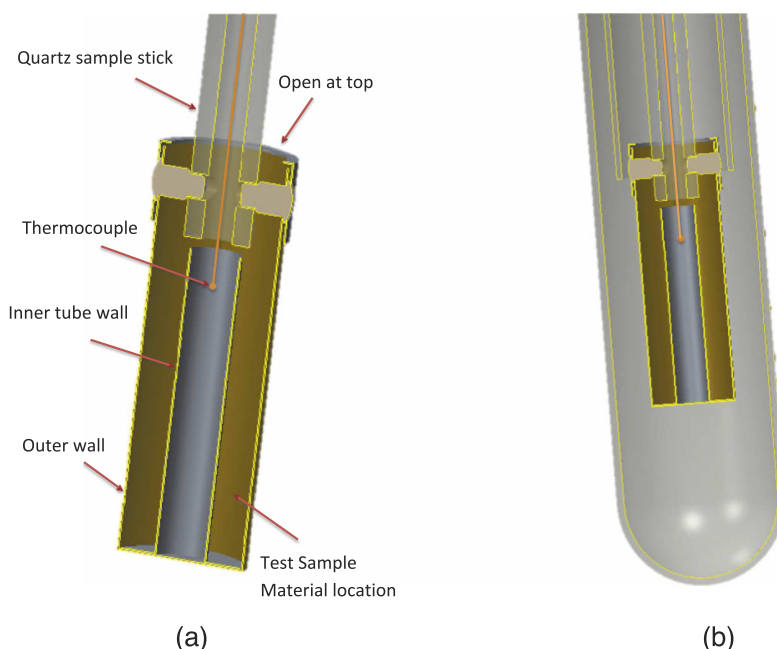


FIG. 4. (a) The sample holder (of wall thickness 0.025 cm) is composed of three main parts; inner Pt tube wall, Pt outer wall, and fused quartz sample stick. The polycrystalline sample is held in the annular cylindrical geometry can. A thermocouple is around the sample to measure the equilibrium temperatures. (b) Sample holder shown in fused quartz tube.

TABLE II. General specification for Micas Furnace Generation I.

Minimum temperature	RT
Maximum temperature Nb	1600 °C
Maximum temperature V	1200 °C
Maximum temperature with fused quartz insert	1000 °C
Inner diameter with standard sample stick	70 mm
Inner diameter with fused quartz tube insert	1.2 in.
Average vacuum inside furnace	5.0×10^{-6} mbars
Thermocouple type <1200 °C	Type K with nickel sheath
Thermocouple type >1200 °C	Type W/C type (bare wire)

the sample. The temperature is measured close to the sample position, and the output is controlled by that temperature by a Partlow temperature controller. The MICAS furnace has safety interlocks that must be within the operating parameters to operate the furnace.

Those safety interlocks are vacuum, water flow, over temperature, and emergency-stop. If any of these interlocks is out of condition, the power supply will not apply any output to the system. For this work, the MICAS furnace operated with a fused quartz tube insert which enabled a wet and dry gas flow of He gas across the sample. The tube setup is made from 3 fused quartz tubes. The outer tube is closed at the end and enables the furnace to operate under a vacuum while flowing a gas across the sample. The middle tube is used to flow the incoming gas, ensuring that the gas flows across the sample, and out of the outermost tube, rather than the gas remaining at the top of the tube. The innermost quartz tube is for holding the sample in place, and also houses the thermocouples, which control the temperature of the furnace. A type K thermocouple was routed through the middle of the fused quartz center tube, and temperature is measured close to the sample position. Table II lists the general specification.

IV. PORTABLE AUTOMATED GAS ENVIRONMENT SYSTEM (PAGES)

A. Overview of the PAGES system

The PAGES delivers measured amounts of up to three gases onto a sample during a neutron scattering experiment. Figures 2 and 5 depict the basic configuration of PAGES. Its applications include the study of methane diffusion, or hydrogen (or other energy significant gases) on high surface-area materials, such as carbon aerogels. Regulated gas pres-

ures up to 100 bars are possible. Using MFCs, standardized buffer volumes, and pressure monitoring, it is possible to characterize the amount of a particular molecular species required to cover a surface, or to saturate a bulk material. Adsorption studies may be done offline, and *in situ* during neutron scattering experiments, allowing scientists to study submonolayer, monolayer, etc., coverages, or bulk uptake. The portability of the apparatus allows it to be used on a variety of SNS instruments, as well as offline laboratories, where user may conduct preliminary tests in preparation for their neutron experiments.

B. PAGES design

The gas handling hardware (valves, tubing, MFCs, buffer volumes, pressure transducers, and vacuum pump) is housed within a metal cabinet, small enough for transport by hand. All gas flow tubing is 1/4 in. diameter, 316 stainless steel, with a pressure rating of 5100 psi. Swagelok™ VCR fittings (metal gasket seals) are used for reliable gas containment and to allow easy installation and removal of individual components. Bulk head VCR fittings are installed on the cabinet exterior for the outside gas connections. The cabinet includes a hinged door with a large window, such that all components are visible during operation, and easily accessible for maintenance. The PAGES system is designed to deliver gas to the sample cell via three separate gas channels as shown in Figure 5. Gas flow is directed through air actuated solenoid valves and is precisely regulated and monitored using MFCs. These components are interfaced to a processor and controller, mounted within the gas cabinet. The control software is written using National Instruments' LabVIEW graphical language. A small diaphragm vacuum pump is housed within the cabinet, allowing automatic pump/purging. The control program fully purges one gas from the system before letting the user add another, to avoid contamination from mixing, or unsafe mixing of incompatible gases. The gas may be supplied either from small lecture bottles housed within the cabinet or from an external gas cylinder. The PAGES control software has a graphical user interface, which shows a virtual gas manifold, with a clearly identified flow path and flow status. A mixture of two separate gases at a time can be delivered to the sample by using the MFC. The gases are mixed prior to entering the sample environment container. Once the gases have been defined, the selected MFC option is activated. The valves required for gas flow to the sample automatically open. PAGES was designed

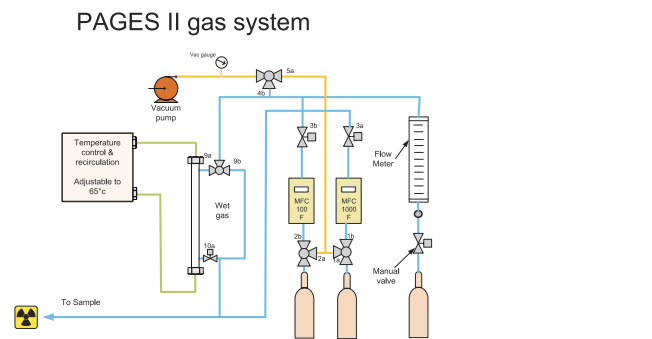


FIG. 5. The PAGES system is connected with three separate gas channels. These channels deliver gas to the sample cell.

to be controlled manually but can also be controlled remotely using a LabVIEW interface program. Manual system control is done by setting the solenoid valve, which controls the gas flow by using a 1000/100 SCCM mass flow controller. Using the GUI, the gas exchanged is easily controlled and monitored. Following the gas change, the gas correction factor for the chosen gas is automatically updated. Two “Thermo CUBE” recirculator water lines are connected from the CUBE to the PAGES cabinet and are labeled “Humidity Cell,” “WATER IN,” and “WATER OUT.” The temperature controller controls the water temperature inside the Thermo CUBE. The relative humidity, in the CUBE, is approximately 90%. The PAGES system can deliver a gas with high relative humidity to the sample.

When wet gas is selected, PAGES automatically selects the correct valves in sequence to start the process, but at this time it does not display the humidity of the sample gas and we have no means of varying the humidity around the sample when the neutron beam is on. The humidity test was done outside the neutron beam time by using humidity probe. Approximately 1 h is required to reach 90% of humidity relative to the atmosphere surrounding the sample can and the inner fused tube, and 1 h when switching back to dry gas to reach 0% relative humidity.

V. EXPERIMENT

The QENS experiments were performed using the BASIS at SNS, ORNL.³¹ The wavelength and energy resolution at the elastic line (full width at half-maximum) were 6.267 Å and 3.4 μeV, respectively. To maintain the sample’s hydration level during QENS measurements, wet gas flow was used. The wet (or subsequently dry) He gas entered the inner fused quartz tube through the inlet and was delivered to the Pt sample holder. The Q range for the experiments was 0.3 Å⁻¹ to 1.9 Å⁻¹. For background measurement, an empty platinum can inside the sample cell system was measured at 11 temperatures between 950 °C and 150 °C under dry He. To study the influence of wet/dry atmospheres on the QENS measurement, two scans were done at 150 °C and 250 °C under wet/dry He conditions. A QENS run was conducted for an annular vanadium standard of thickness 0.127 inside the Pt

can at 50 °C, 35 °C, 26 °C, and RT. Measured spectra were normalized to an annular vanadium standard.

The sample’s thickness and mass were chosen prior to the QENS measurement to reduce the effect of multiple scattering. The sample can be fully hydrated or dehydrated after being inside the SCS for a certain time that depends on the sample. For example, a sample such as lanthanum barium gallate can be hydrated/dehydrated within a few hours.^{16,17} If a sample, such as La_{0.958}Ca_{0.042}PO_{3.979}, needs more time to be charged with proton, it is recommended that the sample be hydrated by post-annealing prior to the QENS experiment.⁹ The initially hydrated sample, La_{0.958}Ca_{0.042}PO_{3.979}•0.021H₂O, was heated inside the QENS sample cell at 150 °C under dry gas for several hours to guarantee no surface water was on the sample’s surface. Spectra were taken at 6 temperatures between 150 °C and 900 °C for the hydrated sample under humid He flow. The sample was then fully dehydrated by purging it with dry He for 10 h at 950 °C. Spectra were again recorded for the dehydrated sample at 4 temperatures between 150 °C and 500 °C in a dry He atmosphere.

VI. DISCUSSION

A quasi-elastic neutron scattering experimental study was performed on proton conductor samples of La_{0.958}Ca_{0.042}PO₄, La_{0.958}Sr_{0.042}PO₄, La_{0.92}Sr_{0.08}PO₄, and Sn_{0.9}In_{0.1}P₂O₇ using the sample cell system described above. The nature of the samples of proton conductor materials required a sample cell system that maintains moisture at an elevated temperature inside the sample under QENS investigation. The sample holder, gas, and optical systems should be carefully considered to reduce the background intensity scattering signal. A good apparatus makes it possible to study the sample’s dynamics without significantly contributing to the sample signal. Figure 6 shows the neutron scattering intensities collected at BASIS for the fused quartz tube and the furnace at room temperature (left), and empty Pt sample holder at 500 °C for $Q = 0.5$ Å⁻¹ (right). The spectra were fit by an elastic δ -function and background contributions.⁹ No clear quasi-elastic (Lorentzian component) appears.

A QENS measurement was done on the SCS and the empty Pt sample holder at BASIS, for $Q = 0.3$ –1.9 Å⁻¹ with

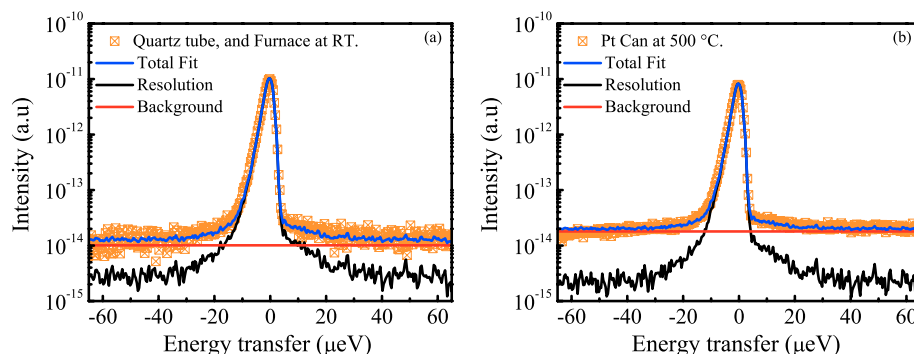


FIG. 6. (a) Neutron scattering intensities at BASIS (log scale) collected for the fused quartz tube and the furnace at room temperature. (b) Neutron scattering intensities collected for empty Pt can inside the fused quartz tube and the furnace at $T = 500$ °C. The spectra at momentum transfer $Q = 0.5$ Å⁻¹ are the orange squares, the corresponding resolution function is shown in black, while the background is in red, and the total fitted curve is shown in blue. (a) and (b) show no clear quasi-elastic components.

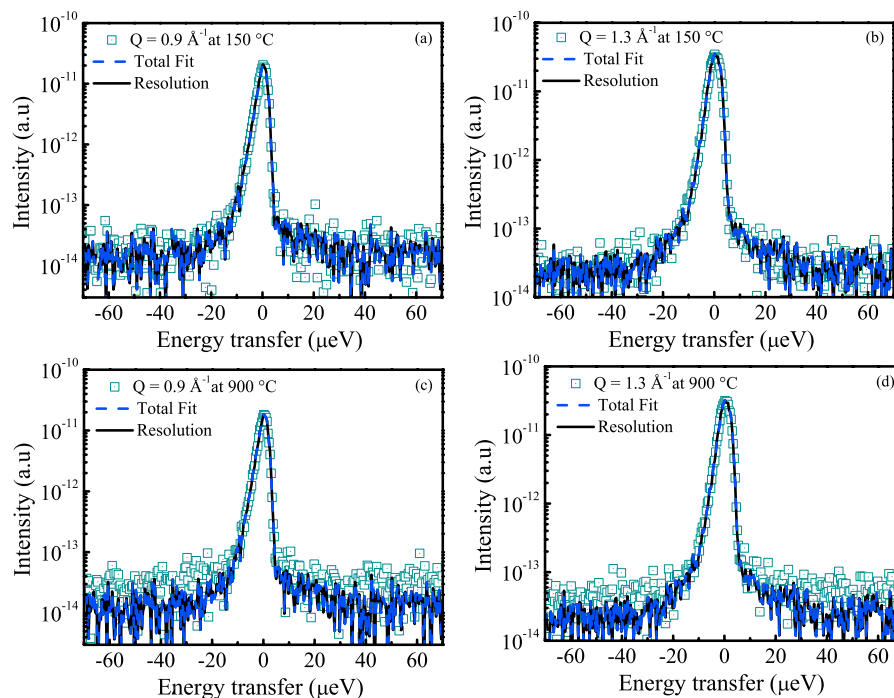


FIG. 7. Neutron scattering intensities (green squares) in log scale, collected for the empty Pt can inside the fused quartz tube and the furnace at $Q = 0.9$ and 1.3 \AA^{-1} . (a) and (b) at $T = 150 \text{ }^{\circ}\text{C}$. (c) and (d) at $T = 900 \text{ }^{\circ}\text{C}$. Corresponding resolution function (black), and the total fitted curve is shown in blue. The spectra show no clear quasi-elastic components and show the stability of the apparatus at elevated temperature.

0.2 step from $T = 950 \text{ }^{\circ}\text{C}$ to $150 \text{ }^{\circ}\text{C}$ under dry He and $150 \text{ }^{\circ}\text{C}$ and $250 \text{ }^{\circ}\text{C}$ under wet He. Figure 7 depicts the neutron scattering intensities for the empty sample holder in the SCS at BASIS, for $Q = 0.9$ and 1.3 \AA^{-1} at $T = 150$ and $900 \text{ }^{\circ}\text{C}$. The SCS's thermal stability is clearly shown with no clear quasi-elastic component appearing at elevated temperatures. A vanadium neutron scan was done inside the sample holder as a reference at RT.

Neutron scattering was measured for the SCS under two different conditions: dry flowing He and humid flowing He gas. Neutron scattering intensities were collected for the empty Pt sample holder in the sample cell system under dry and wet He at $150 \text{ }^{\circ}\text{C}$ and $250 \text{ }^{\circ}\text{C}$. Figure 8 shows the SCS's neutron scattering intensities at $250 \text{ }^{\circ}\text{C}$ for $Q = 0.9 \text{ \AA}^{-1}$. As expected, the measurement showed no difference in the neutron signal between wet and dry He with no quasi-elastic signal contribution from SCS. For comparison, Figure 9 shows the hydrated 4.2% Ca-doped LaPO_4 sample inside the platinum can in SCS

under wet He at $250 \text{ }^{\circ}\text{C}$ (for $Q = 0.3$ and 0.5 \AA^{-1}), which clearly shows a quasi-elastic component from proton diffusion in the sample.

The neutron scattering signal from a proton is primarily incoherent. It gives information about the self-diffusive motions. The hydrated sample can be separated into elastic δ -function, quasi-elastic (Lorentzian), and background contributions as shown in Figure 9. The quasi-elastic component broadens with increasing temperature and increasing Q , as opposed to the result found earlier⁹ where the signal from the dehydrated sample was elastic, exhibiting no broadening beyond the instrumental resolution. QENS data were collected at 150, 250, 350, and $500 \text{ }^{\circ}\text{C}$ to obtain further information on proton conduction and to examine models for the mechanism of proton diffusion in the lower temperature regime where the dynamics were found within the time window accessible by BASIS. The mean residence time $\tau(\text{ps})$, mean jump distance $\ell(\text{\AA})$, mean-square displacement $\langle u^2 \rangle^{1/2}$, self-diffusion

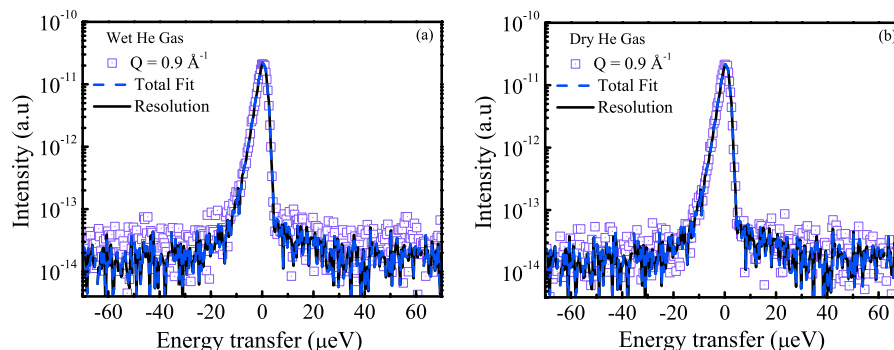


FIG. 8. Neutron scattering intensities shown in log scale (violet square) collected for the empty Pt can inside the fused quartz tube and the furnace at $Q = 0.9 \text{ \AA}^{-1}$ at $T = 250 \text{ }^{\circ}\text{C}$. (a) The spectrum obtained with flowing He through H_2O bubbling systems. (b) Flowing dry He. No significant difference in the neutron signal is seen between wet and dry He. Corresponding resolution function (black), and the total fitted curve is shown in blue.

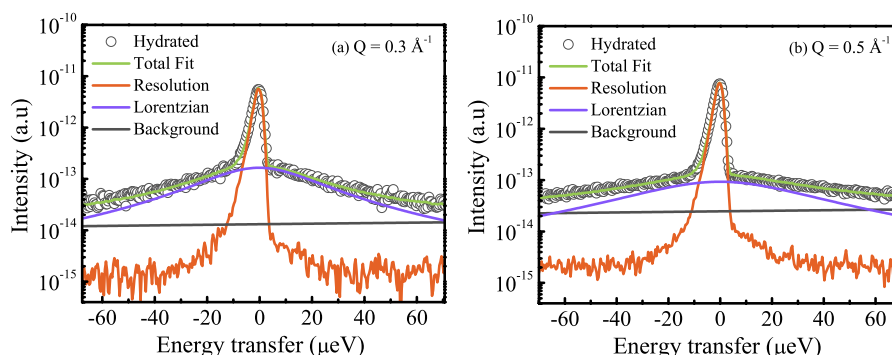


FIG. 9. Hydrated 4.2% Ca-doped LaPO_4 quasi-elastic spectra (log scale) collected at BASIS (gray symbols) at $T = 250^\circ\text{C}$. The spectrum obtained with flowing He through H_2O bubbling systems (a) $Q = 0.3 \text{ \AA}^{-1}$ and (b) $Q = 0.5 \text{ \AA}^{-1}$. Corresponding resolution function (orange), the Lorentzian quasi-elastic component is shown in violet, the background is in gray line, and the total fitted curve is shown in green.

coefficient $D(\text{cm}^2/\text{s})$, and activation energy $E_a(\text{eV})$ were estimated from the half-width at half-maximum of the Lorentzian function at each temperature.⁹ The QENS experiment revealed a fast dynamical process below 500°C that was not observed by EIS. The activation energy of the fast proton diffusion is 0.09 eV in the temperature range from 150°C to 500°C .

Spectra of the dehydrated 4.2% Ca-doped LaPO_4 sample were recorded at 4 temperatures between 150°C and 500°C in a dry He atmosphere. The dehydrated sample exhibited little or no temperature dependence beyond a slight reduction in intensity due to increased Debye-Waller vibrational motion.

VII. SUMMARY

Maximum operational temperature has been a common limitation on the use of sample cells and cell holders, where it is often the case that studies are limited to temperatures below 300°C . This is attributable to the use of aluminum in designing instrumentation. In this work, we presented a new apparatus that has been designed and built at Oak Ridge National Lab to address this issue. It has been tested and successfully used in a series of experiments at temperatures up to 950°C , with the ability to switch between humid and dry flowing gas conditions in addition to controlling the flow of various gases.

The apparatus consists of a SCS coupled with a PAGES that controls the flow of gas around the sample and the MICAS furnace. The advantages of this design are that (1) unlike previous cells, this one avoids the buildup of water vapor pressure that could lead to leakage and undesirable beam contamination or cell deformation by opting for an open design, as opposed to sealed cans that have been used in the past. (2) The use of platinum combined with fused quartz in place of aluminum enables us to probe a much wider range of temperature reaching 950°C . (3) The ability to control atmospheric conditions through different humid and dry gas flows.

The sample cell system and PAGES presented here can be used over wide measurement ranges under different temperatures and various operating conditions, allowing chemical, dynamical, and physical changes *in situ* to be studied. In our case, we have used this apparatus to facilitate QENS measurements of proton conductors at elevated temperatures.

Two quasi-elastic neutron scattering experiments demonstrated SCS's potential. The first experiment was done on an

empty sample holder inside the SCS at different temperatures between 150°C and 950°C under dry He and at 150°C and 250°C under wet He. The second experiment was conducted on a sample placed within the platinum sample holder inside the SCS.

From the first set of experiments on the SCS system, we observed no detectable quasi-elastic signal from SCS, showing that the presence of the SCS does not contribute a significant noise to the sample signal. The SCS was investigated under neutron scattering under two different conditions: dry flowing He and humid flowing He. In both cases, there was no sign of a quasi-elastic signal attributable to the SCS. From the second set of experiments, we were able to maintain the sample hydration and study the sample at an elevated temperature up to 900°C and we were able to dehydrate the sample in the SCS.

The SCS and PAGES can be used in a variety of neutron beam lines, for example, powder diffraction with suitable sample holder material such as vanadium or fused quartz. A possible modification to the design would enable the system to accommodate special sample environments, such as *in situ* pressure cells.

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