PNNL-33842

Investigating Hydrogen Isotope Exchange Reactions on Lithium Aluminate Pellets in TPBAR

FY22 Report

January (2023)

Jiyoung Son
Xiao-Ying Yu

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99354

Abstract

We developed a novel operando Raman spectroscopy method for investigation of hydrogen (H) isotope exchange reactions in the lithium aluminate (γ-$LiAlO_2$) that allows modeling of tritium behaviors in high temperature and in an irradiated sample. The lithium aluminate pellet is a main component in the Tritium-Producing Burnable Absorber Rod (TPBAR). We used deuterium (^2H or D) as a surrogate to simulate tritium (^3H or T). We used a surface analysis tools *in situ/operando* Raman spectroscopy to observe the transformation OH and OD compositional changes. We also used ToF-SIMS to analyze the lithium aluminate pellet control sample to build the baseline for future in situ/operando analysis. To conduct operando Raman spectroscopy, we developed a custom reaction cell with a detachable micro heater using microelectromechanical systems (MEMS) and 3D printing techniques. Multiple versions were developed and tested. Using the new reaction cell, we demonstrated operando Raman spectroscopy of water (H_2O) and deuterated water (D_2O) with nitrogen (N_2) exposure onto the lithium aluminate ($LiAlO_2$) pellet specimen, respectively, using a wet gas injection setup. We also successfully developed a detachable microheater that can heat up to ~250°C for ~90 mins. The Raman spectra did not show clear H_2O and D_2O characteristic peaks, which indicates that introducing H_2O and D_2O onto the surface of the pellet is challenging due to its dense structure nature. Our efforts suggest that various improvements are needed, such as increasing reaction cell operating gas pressure and thinning pellet sample thickness, to obtain meaningful measurements.

Summary

We developed an in situ/operando Raman spectroscopy setup to investigate the isotope exchange behaviors in γ-$LiAlO_2$ pellet used in TPBAR. ToF-SIMS was also used to obtain composition information of γ-$LiAlO_2$ pellet.

There were three aims in this project: **1**). Fabricate a reaction cell compatible with Raman spectroscopy and integrable to the existing SIMS heating stage;**2**). Use *in situ/operando* Raman to study the isotope exchange rates and to understand the hydrogen behaviors in γ-$LiAlO_2$; and **3**) Use *in operando* heating in ToF-SIMS to study the isotope exchange reaction products.

These aims were used to answer the following questions: **1**) Are there isotope effects in γ-$LiAlO_2$ pellet? If so, what are the isotope exchange rates in different temperature conditions? **2**) Is there an anomalous isotope difference in the hydrogen exchange, assuming that the isotope exchange rates are different in H/D and D/H process?

We utilized MEMS and 3D printing techniques to develop the new Raman reaction cell. We developed multiple versions of reaction cells. The cell contains multiple layers, and each has a specific function including a reaction layer (top layer), flexible sealing layer (middle layer), and microheater function layer (bottom layer).

We also successfully developed a detachable microheater using photolithography and lift out microfabrication techniques in the cleanroom. The microheater was tested for maximum temperature and endurability. The test data showed that the new system can sustain heating up to ~250°C for ~90 min. With the completed reaction cell prototype, we performed Raman experiments while introducing H_2O and D_2O wet gas on the surface of $LiAlO_2$ pellet. The H_2O and D_2O wet gas injection setup utilized two glass flasks, polytetrafluoroethylene (PTFE) tubing, PEEK fittings, and PEEK gas valves. The result suggests that the reaction cell and the pellet sample preparation need improvements such as reaction chamber for high pressure and thinner pellet sample.

The newly developed Raman setup showed the potential to provide direct observations of hydrogen isotope exchange reactions and to study the isotope exchange rates in γ-$LiAlO_2$ substrate under unirradiated conditions in the future.

Acknowledgments

The authors are grateful for the support from the Tritium Technology Program for support of the work performed in this report. The authors would like to thank the Pacific Northwest National Laboratory (PNNL) Nuclear Processing and Sciences Initiative (NPSI) – Laboratory Directed Research and Development (LDRD) fund for the initial investment to prepare for the Task Specific Procedure preparation to transfer irradiated samples for analysis at the W. R. Environmental Molecular Sciences Laboratory (EMSL) facility at PNNL. The authors are indebted to David Senor and Andrew Casella for discussions and suggestions on sample selections. The authors would like to thank Anthony Guzman for pellet sample preparation and Brian O'Callaghan for instrument assistance. Raman spectroscopy analysis were performed in the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored for the Department of Energy located at PNNL. Prototyping process was done in the Instrument Development Laboratory of EMSL, and microfabrication process was performed in the cleanroom in EMSL. PNNL is operated by Battelle for U. S. Department of Energy (DOE) under the contract DE-AC05-76RL01830. Xiao-Ying Yu would like to acknowledge the Oak Ridge National Laboratory (ORNL) for support of her time to complete the report. ORNL is managed by UT-Battelle, LLC under the contract DE-AC05-00OR22725.

Acronyms and Abbreviations

Al	Aluminum
Bi	Bismuth
CAD	Computer-Aided Design
D	Deuterium
D_2O	Deuterium Oxide (Heavy Water, Deuterated Water)
H_2O	Hydrogen Oxide (Water)
LiAlO2	Lithium Aluminate
Li	Lithium
MEMS	Micro Electromechanical Systems
PNNL	Pacific Northwest National Laboratory
T	Tritium
TPBAR	Tritium Producing Burnable Absorber Rods
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry

Contents

Figures

1.0 Introduction

1.1 Background

The dynamic behavior of hydrogen (H), such as diffusion, retention, and re-emission of H isotopes in bulk and at the surface of tritium breeding materials in fusion reactors, has received extensive attention in fundamental and application views [1, 2, 3, 4]. Previously there has been limited effort [5] to demonstrate *in situ*/operando Raman spectroscopy to observe the H isotope exchange reactions and to quantify the isotope exchanges rates at different temperatures in proton conducting oxides (Figure 1C). The isotope exchange rates in the D-H exchange and H-D exchange are different, indicating there is an anomalous isotope effects during the hydrogen isotope reactions. Different from high-temperature protonic ceramic conductor, tritium can transport through substitutional tritium diffusion and oxygen-tritium diffusion in tritium breeding materials. Therefore, it is important to study the dynamic behavior of hydrogen isotopes in tritium breeding materials, specifically the lithium aluminate pellet from TPBAR, by studying the hydrogen isotope exchange reactions to understand gaseous transport and isotopic exchange and provide insights into the mechanism of tritium separation and production.

2.0 Technical Methods and Materials

2.1 Development Workflow

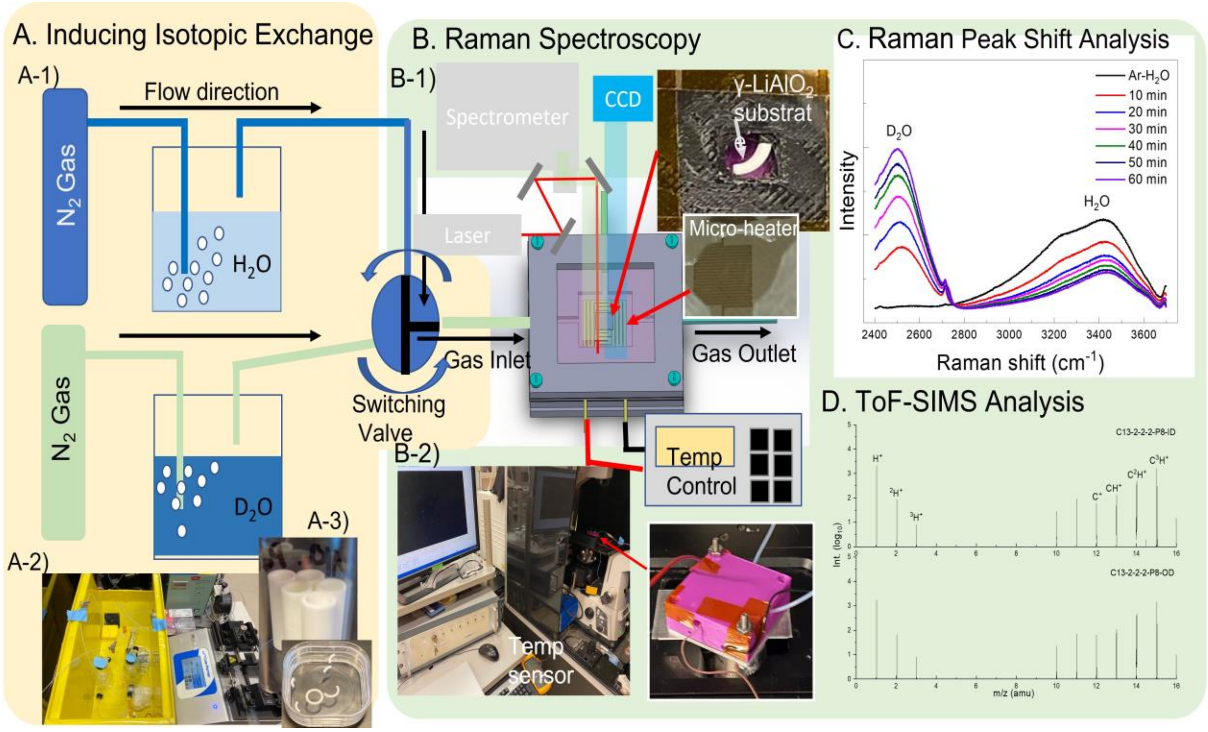

Figure 1. Workflow of hydrogen isotope exchange reactions in the γ-$LiAlO_2$ pellet using a novel reaction cell: A-1) the controlled atmospheric setup, A-2) photo of the implemented setup, B-1) the microfluidic/MEMS based reaction cell for in situ/operando heating Raman spectroscopy, B-2) the developed reaction cell, C) representative Raman spectra of H isotope exchange reactions after changing the atmosphere from N_2/H_2O to N_2/D_2O, and D) sample SIMS spectra from an irradiated pellet.

The objective of this project is to use *in situ and operando* Raman spectroscopy and *in operando* ToF-SIMS to characterize the isotope exchange reactions in γ-$LiAlO_2$ to understand the dynamic behavior of hydrogen isotopes in the bulk and at the surface of pellet under elevated temperatures ranging from 25 – 400 °C in this project.

We designed the experiment process in three parts: **1**) inducing in situ isotopic exchange of $LiAlO_2$ substrate using H_2O and D_2O with nitrogen (N_2) as a carrier gas (Figure 1A-1, 2); **2**) developing the custom reaction cell (Figure 1B-1) that is compatible with *in operando* Raman measurements; and **3**) performing *in operando* heating analysis to determine hydrogen isotopes using Raman (Figure 1C) and to obtain mass spectra and images in ToF-SIMS (Figure 1D) of the retrieved $LiAlO_2$ pellet materials.

There were four tasks: **I**) Fabricate a transferrable reaction cell for Raman spectroscopy; **II**) Perform in situ Raman spectroscopic measurements to study H isotope exchange reactions on the microfluidic device and quantify reaction rates; **III**) Perform *in operando* heating analysis in ToF-SIMS to characterize the surface species before and after H isotope exchange reactions in

Raman to understand the isotope exchange reactions on the surface of γ-$LiAlO_2$; and **IV**) Project management.

2.3 Reaction Cell Development

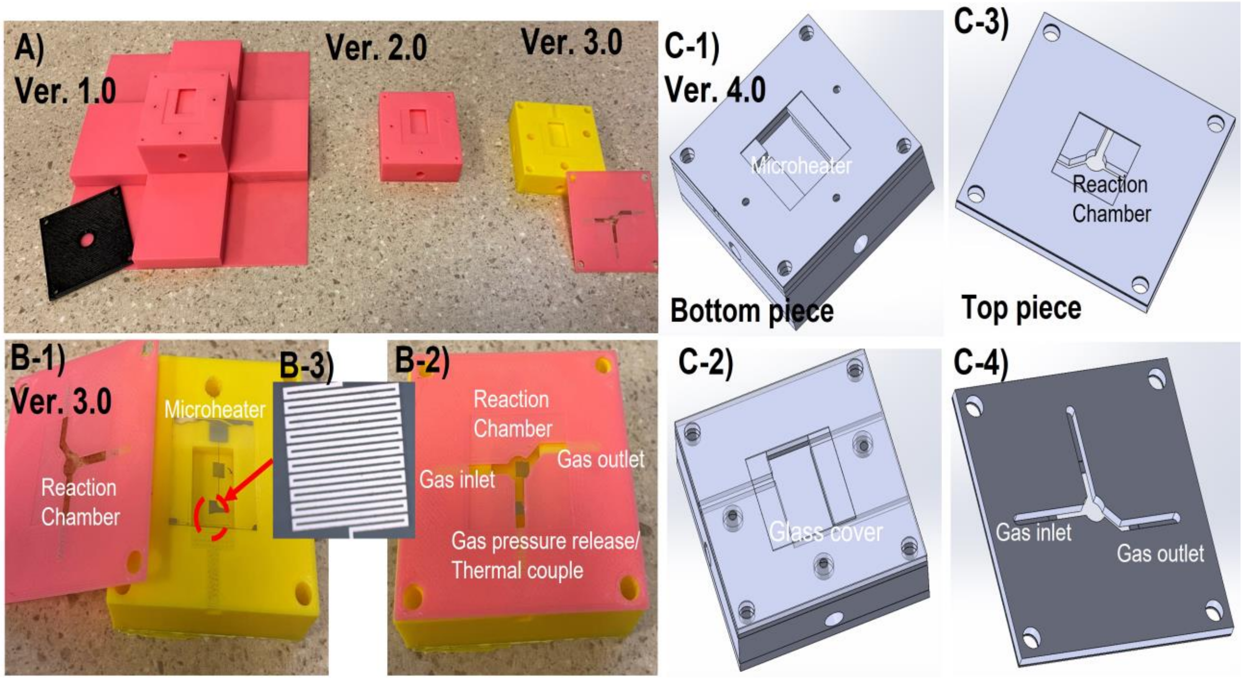

Figure 2. Reaction cell design process: A) different versions of the heating cell design, B) detailed reaction cell including upper layer, bottom layer, and detachable microheater of the reaction chamber, and C) CAD design showing four views of the prototype.

In task **I**, several reaction prototypes have been made using CAD design, 3D printing MEMS technique. Key results are show in Figure 2. The heating cell contains a multi-layer structure, which provides inter-connected gas flow channel, a reaction cell, and microheater structure (Figure 2C). Inside the reaction chamber, there are three gas flow channels for inlet, outlet, and pressure release, respectively (Figure 2B-2, 2C-4). On the top of the reaction chamber, there is a transparent glass window to seal the chamber. There is a microheater on the bottom structure of the cell (Figure 2-B-1, C-1). There are three channels for DC power for positive and negative lines and a thermocouple in the bottom cell structure (Figure 2B-1, 2C-2).

The $LiAlO_2$ sliced sample with a dimension of approximately $4 \times 3 \times 2$ mm^3 was placed in the middle of the reaction chamber, while the top of the microheater surface was used for heating sample. Top and bottom structure was sealed with the polyurethane membrane sealer to form an enclosed chamber, respectively, making it adaptable to the Raman spectroscopy setup (Figure 2B-2). The whole structure is clamped as one structure with bolts and nuts (Figure 2B-2). The structure is detachable after Raman experiments, and it allows easy access to the pellet sample for *in operando* heating experiments in ToF-SIMS after Raman, thus obtaining correlative information.

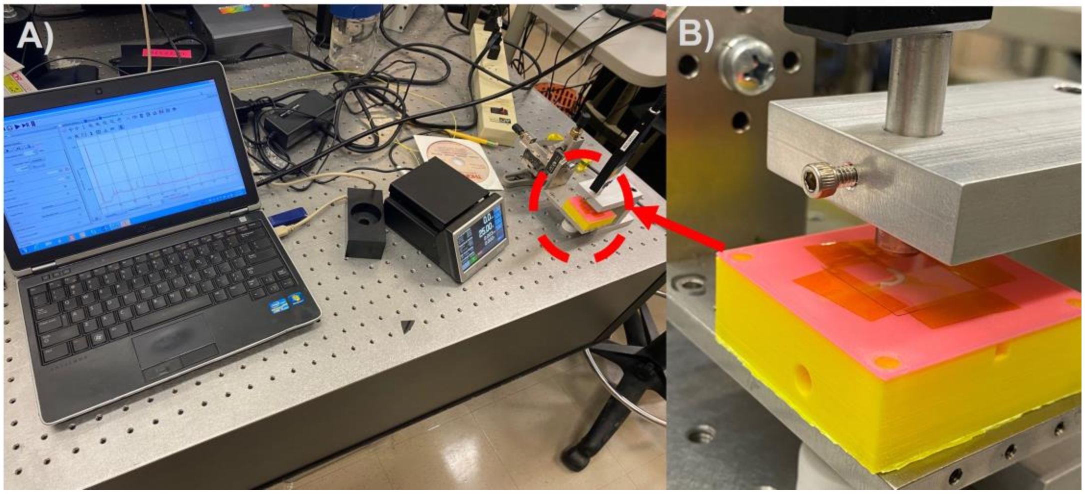

Figure 3. Raman spectroscopy test for possible background interference A) overview of the testing setup, B) close-up of the cell prototype on the Raman sample stage.

We conducted a Raman spectroscopy background test with an experimental setup shown in Figure 3. The purpose of this experiment was to investigate possible background interference from spectral shift in Raman data. We loaded a piece of $LiAlO_2$ sample in the reaction chamber of the prototype reaction cell; and we looked for expected Raman peaks (i.e., Li, Al, and LiO_2). The spectral profile is compared with reference ones acquired from a normal Raman sample holder using the same setup to determine if there are possible differences from the materials of the new reaction cell.

2.3.1 Microheater Development

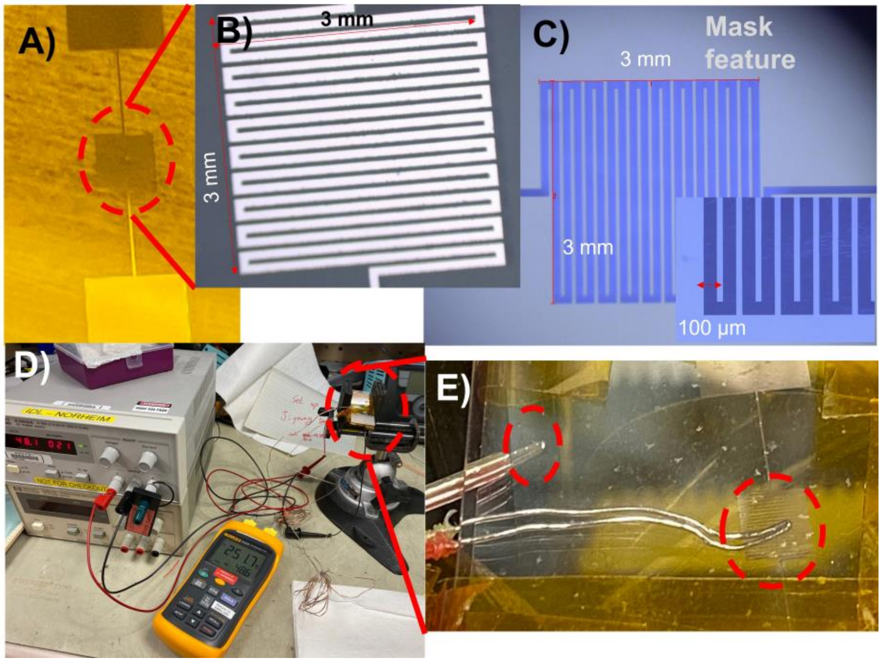

Figure 4. The fabricated microheater and testing setup: A) the fabricated microheater on a glass substrate, B) close-up view of the microheater, C) mask feature for the UV exposure process, D) testing setup for the microheater, and E) two temperature measure locations on the back surface of the fabricated substrate.

The microheater was developed using photolithography and lift-out technique on the surface of glass substrate (22 mm × 22 mm × 200 nm) shown in Figure 4-A. The dimension of the heater design was decided based on maximal heating surface exposure of the sliced pellet material.

The standard photolithography was conducted to develop heating features. First, the feature was developed using UV exposure on photoresist (Figure 4-C). Then titanium (210 nm) and gold (30 nm) layers were sputter coated using the Denton Vacuum sputtering system. Lastly, excessive metal materials were lifted out, which made the final feature on the glass substrate (Figure 4-B).

The heating capability test of the heater was conducted separately for max temperature and endurability (Figure 4-D). DC voltage source and thermal couple sensor was utilized for this test. Two leads of thermal couples were place the back side of the microheater glass substrate which were able to measure the center of heater area and edge of the heater substrate (Figure 4-E). The heater was powered up DC voltage up to 50V. The temperature of the heater was recorded util its failure which also gives its endurance time.

2.4 *In situ and operando* Raman Experimental Setup

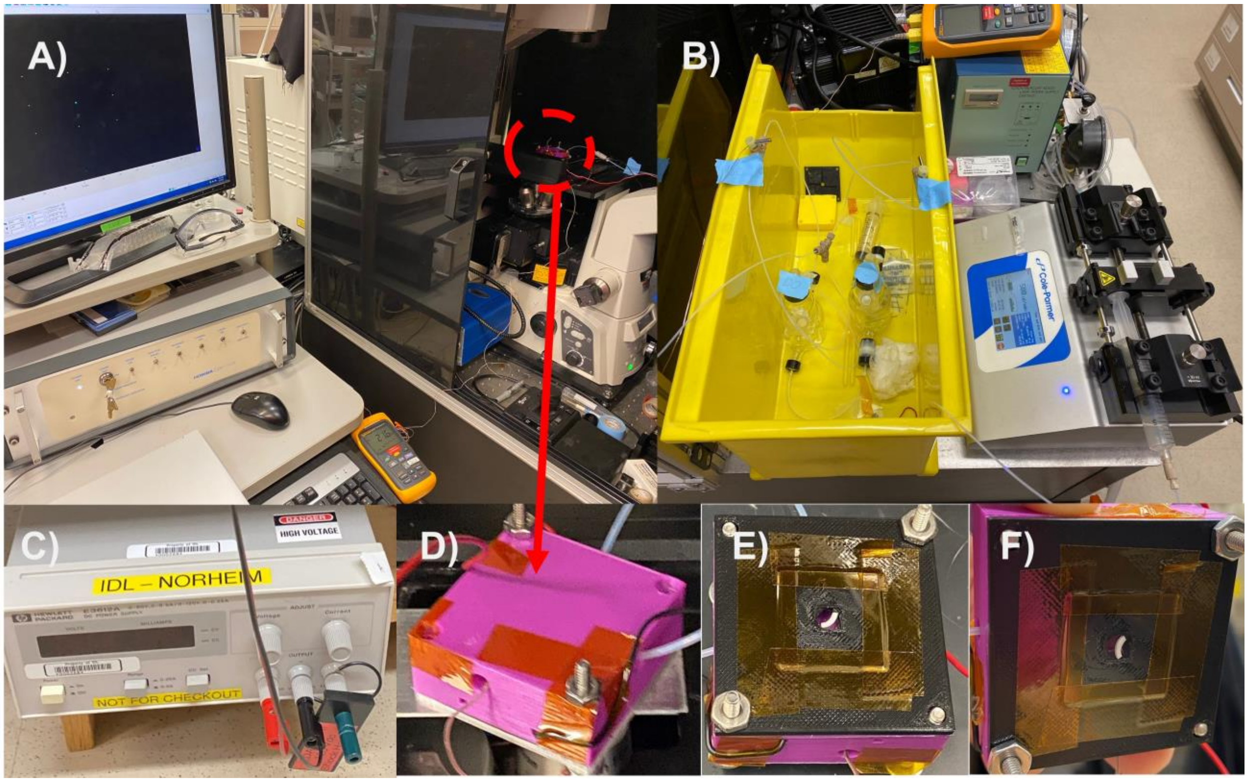

Figure 5. A) *In situ/ operando* Raman experiment setup overview, B) H_2O and D_2O wetted N_2 gas injection setup, C) DC voltage source for microheater, D) close-up look of the implemented reaction cell on the Raman sample stage. E-F) close-up top view of sample loaded reaction cell.

In task **II**, *in situ/ operando* Raman spectroscopy experiments were performed to demonstrate isotope exchange reactions using the prototype cell. Mixtures of N_2/H_2O and N_2/D_2O were used Figure 5 shows a photo of the experimental setup. A sliced $LiAlO_2$ sample was loaded into the reaction chamber (Figure 5-E, F); and the external gas line was permeated using two different wet N_2 gases that include H_2O and D_2O, respectively, (Figure 5-B) for certain period of times (i.e., 30 min., 1 hr., 2hr.). The H_2O and D_2O wet gas injection setup utilized two glass flasks, polytetrafluoroethylene (PTFE) tubing, PEEK fitting, and PEEK gas valves. A switch valve was used to alternate between H_2O and D_2O conditions (Figure 5-B). During gas exposure, Raman spectra were acquired for different times (i.e., 30 min, 1 hr., and 2 hr.) to determine if the current setup was adequate or not.

A set of standard pellet samples covered with droplets, namely ~40 µL of H_2O and D_2O, were also analyzed using Raman to verify the effectiveness of the reaction cell in terms of gas exposure. These samples were placed under the droplet for 15 min and 30 min before spectral acquisition.

2.5 ToF-SIMS Analysis of the Pristine Pellet Sample

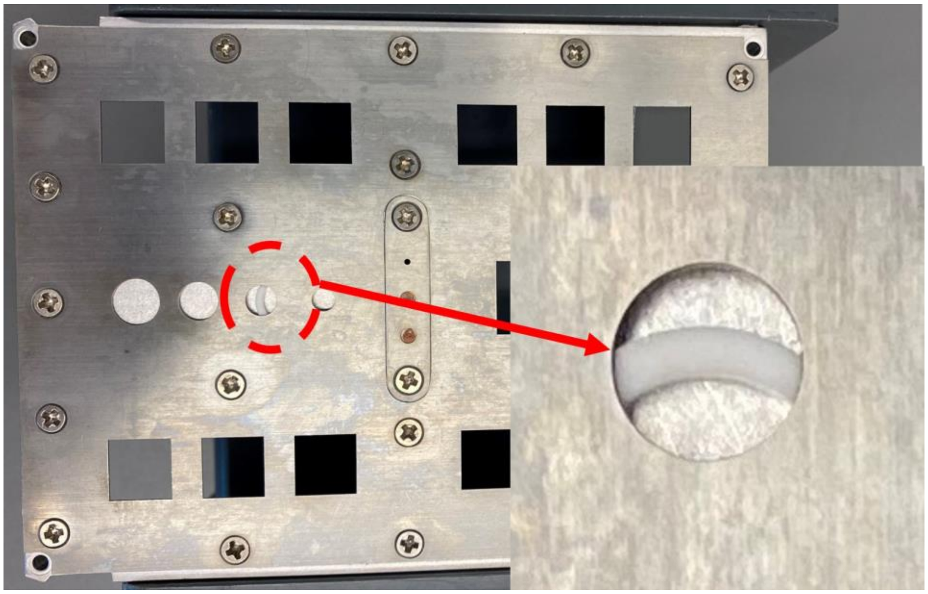

Figure 6. A $LiAlO_2$ sample loaded in the ToF-SIMS back-mount sample holder

ToF-SIMS V spectrometer (IONTOF, BmbH, Münster, Germany) was used for providing information on the chemical composition of a pristine $LiAlO_2$ pellet sample as control. The scanning area size was 250 µm × 250 µm using the 25 keV Bi^+ primary ion beam. The scan cycle was 60 scans, and the main vacuum chamber was 3.9E-8 mbar.

3.0 Results and Discussions

3.1 Reaction Cell Fabrication

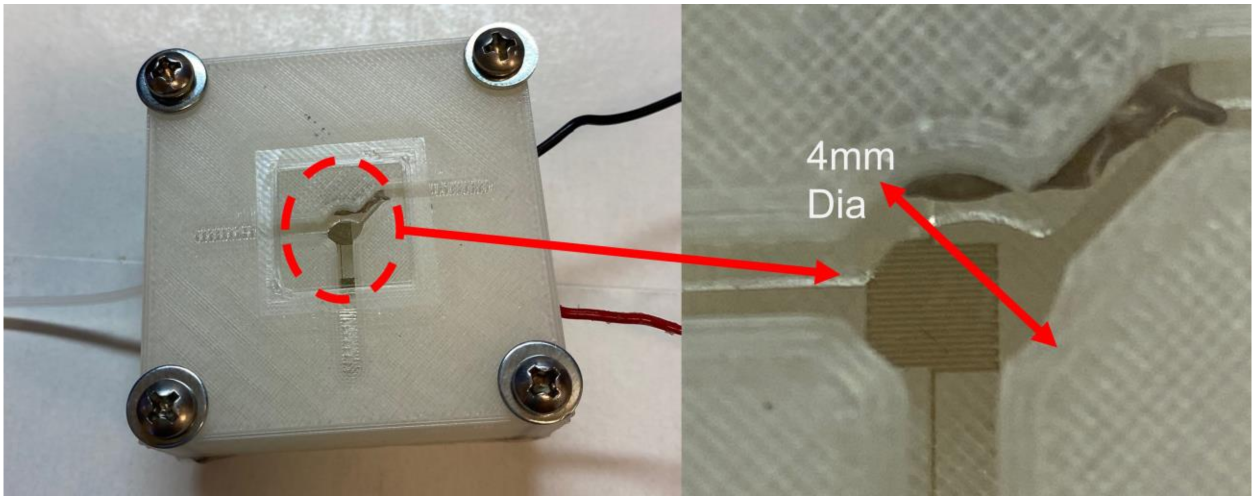

Figure 7. The prototype reaction cell contains a microheater and DC voltage power connection.

Multiple reaction cell prototypes were constructed, and each cell contained a detachable microheater and interconnected gas channels. The reaction chamber was sealed and placed on a glass substrate. The chamber layer and the bottom microheater layer were clapped with a flexible polyurethane membrane. DC power cables (+/-) are fed in the bottom structure; and they were physically contacted on the two microheater contact areas, respectively.

3.1.1 Microheater

Fabricated microheaters were tested for endurance under 50 V. The maximal temperature of the center heater feature had been kept at ~254°C for 90 min, while the DC power and current were kept at 48.1V and 0.21A, respectively. The maximal temperature ramping time was less than ~2 min from 23 to 245°C. The average temperature of the edge of the heater substrate was ~48°C. The heater could go longer than 90 min. However, the voltage of the last few minutes of testing was slightly increased by 0.6 V. This may cause overheat and burning up of the heating element. In the next step, longer heating can be tested.

3.2 Preliminary Raman Spectroscopy Results

3.2.1 Raman test for possible background interference

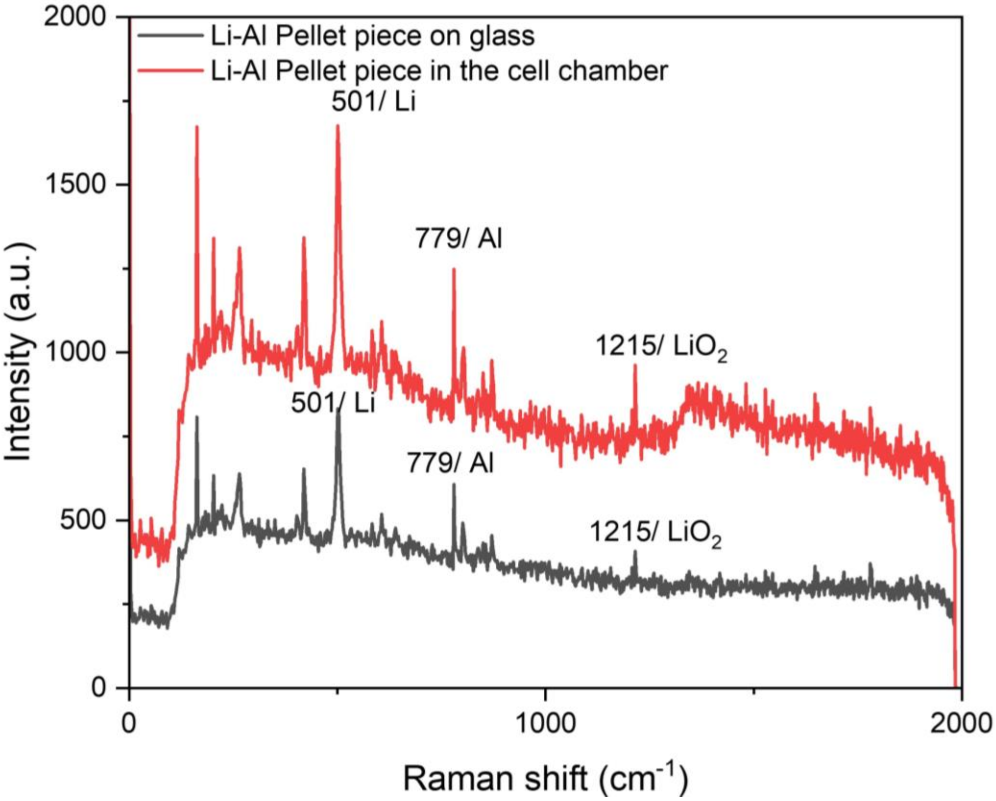

Figure 8. Raman spectroscopy testing result of the $LiAlO_2$ pellet sample.

Figure 8 shows typical peaks of the $LiAlO_2$ pellet. Measurements of the pellet were made between a glass slide as the reference (black) and in situ/*operando* testing cell (Red). Even considering intensity difference, spectral features appear identical with prominent peaks, such as Li (501 cm^{-1}), Al (779 cm^{-1}), and LiO_2 (1215 cm^{-1}). This result suggests that the cell chamber materials have no interference to the pellet measurements using Raman.

3.2.2 *Operando* Raman with exposure of mixtures of H_2O and N_2 and D_2O and N_2

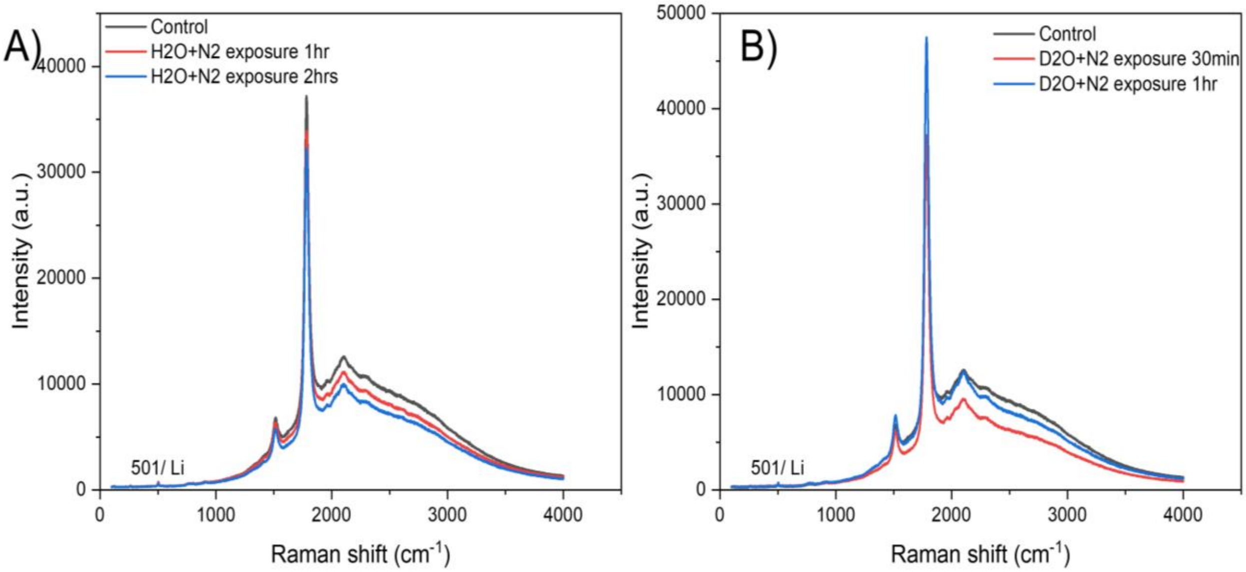

Figure 9. Raman spectra of *operando* Raman of the $LiAlO_2$ pellet exposed to H_2O and N_2 (A) and D_2O and N_2 (B).

Raman spectra (Figure 9) show *operando* Raman spectroscopy results using the prototype reaction cell. The mixed H_2O and N_2 and D_2O and N_2 gases were used to expose on the pellet sample, respectively. Different gas exposure times were used, such as ranging from 30 min to 2 hrs. The spectral results were almost identical without H_2O (~3200 cm^{-1}) and D_2O (~2500 cm^{-1}) profile peaks. These results represent current gas exposure process was not efficient enough to introduce H_2O and D_2O on the surface of the sample. This can be improved by longer exposure or higher-pressure gas exposure. These improvements require reinforcement of cell structure and gas inlet fittings.

3.2.3 Raman Spectroscopy of the standard pellet with H_2O and D_2O

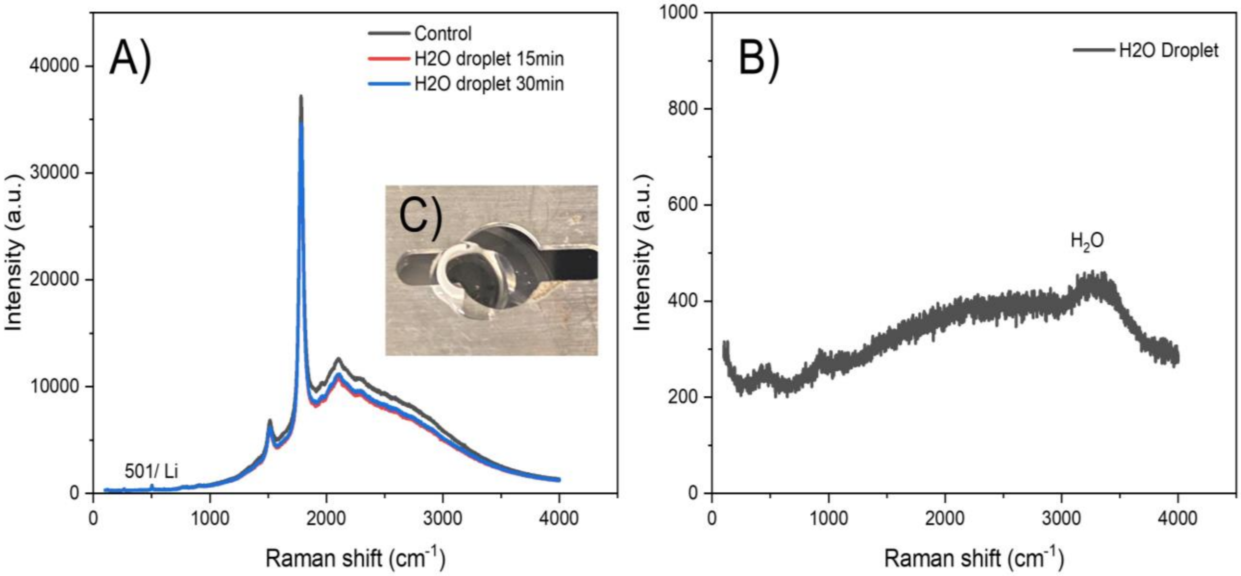

Figure 10. Raman spectra using the standard pellet: A) the control sample with H_2O droplet exposure after15 min and 30 min respectively, B) H_2O droplet, and C) a photo showing the pellet sample with H_2O droplet on the glass slide.

Figure 10 shows Raman spectral results. The spectral results shown in Figure 10-B demonstrate that H_2O (~3200 cm^{-1}) can be detected. However, there were not significant signals of D_2O on the pellet surface after 15 min and 30 min. This observation indicates that introducing D_2O on the sliced pellet sample will require more effort.

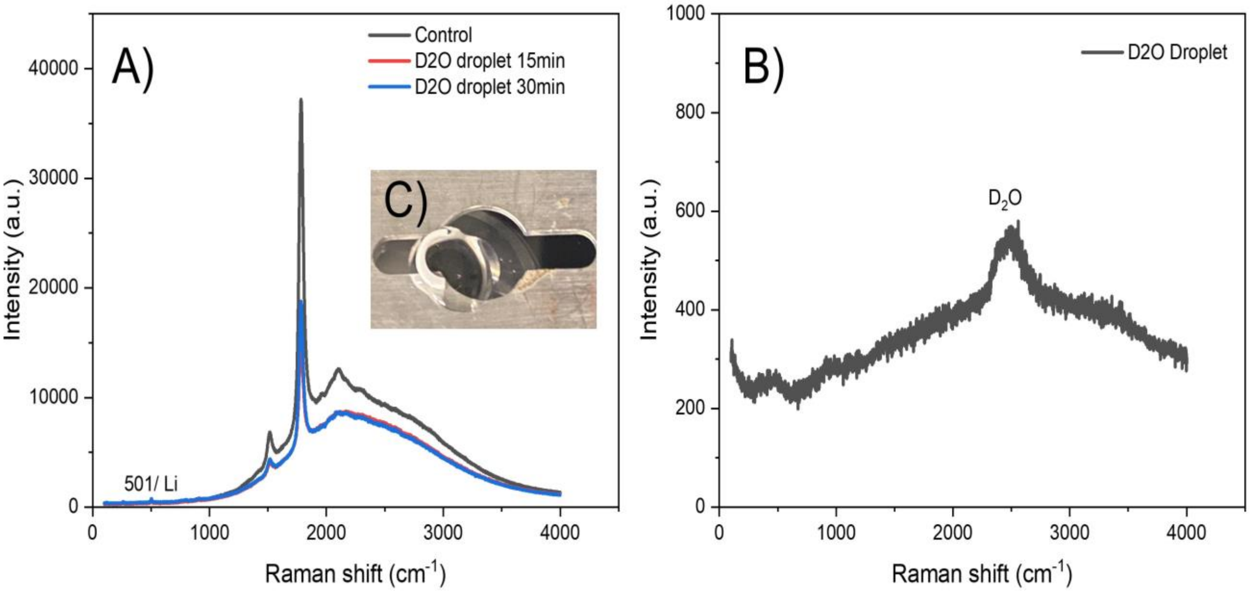

Figure 11. Raman spectra using the standard pellet: A) the control sample with D_2O droplet exposure after15 min and 30 min respectively, B) D_2O droplet, and C) a photo showing the pellet sample with D_2O droplet on the glass slide.

Figure 11 shows Raman spectral results. The spectral results shown in Figure 11-B demonstrate that D_2O (~2500 cm^{-1}) can be detected. However, there were not significant signals of D_2O on the pellet surface after 15 min and 30 min. This observation indicates that introducing D_2O on the sliced pellet sample will require more effort.

3.3 ToF-SIMS Spectral Results of the Reference of Pellet Sample

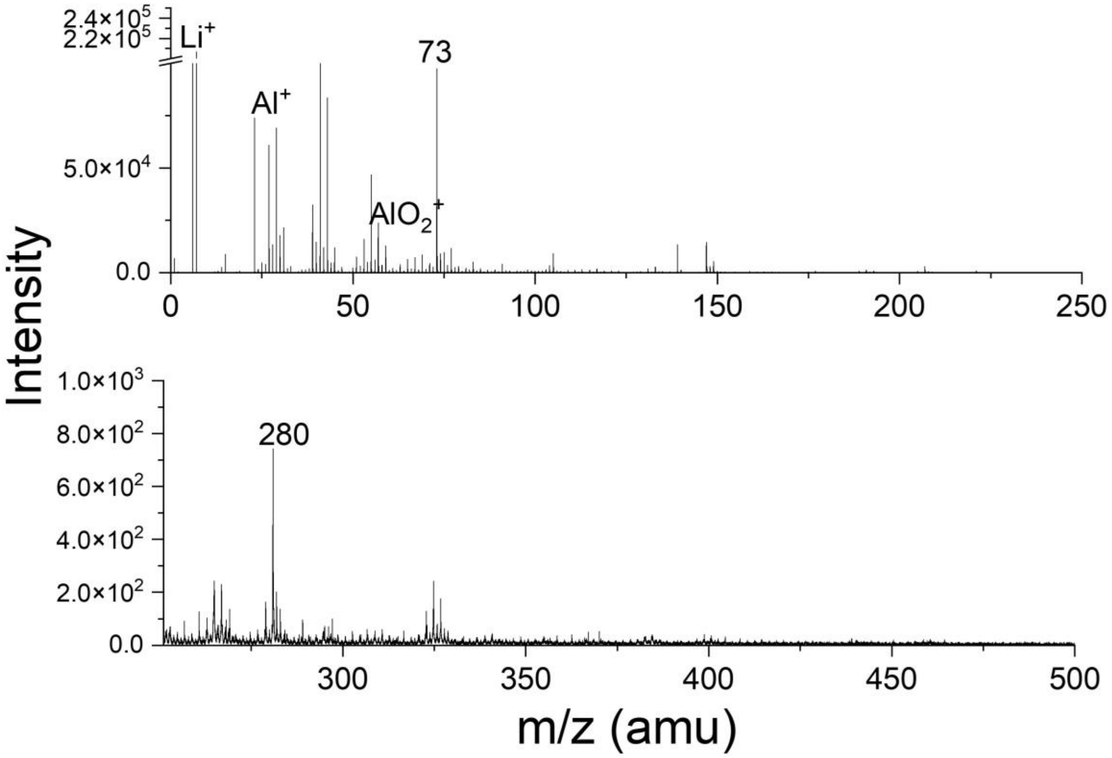

Figure 12. ToF-SIMS spectra of the pristine $LiAlO_2$ pellet sample in the positive ion mode.

We acquired reference ToF-SIMS spectra data of pellet samples in the positive ion mode (Fig. 12). This result shows that ToF-SIMS can provide detailed chemical information of the pellet surface. Data will be used as reference, and they will be compared with samples after exposure of H_2O/ D_2O and N_2 gas mixtures. The negative mode measurements were tried; however, results were not good, likely due to charging and beam effects. Additional experiments are needed to use charge compensation and obtain better results.

4.0 Conclusions and Future Work

We developed a prototype heating cell for in-situ/ operando Raman spectroscopy to study hydrogen exchange reactions. The cell prototype was fabricated using MEMS and 3D printing techniques. We also successfully developed a detachable microheater which can heat up to ~250°C for ~90 mins. Using the completed prototype reaction cell, we conducted operando Raman spectra experiments while inducing H_2O and D_2O wet gas on the surface of $LiAlO_2$ pellet. However, the Raman spectral results did not show characteristic H_2O and D_2O peaks, which indicates that the experimental setup needs improvement. The challenge is due to the dense structure of the pellet material and also likely insufficient reaction time.

The Raman spectra of standard pellet exposed to H_2O/ D_2O droplets have demonstrated that the approach can detect H_2O and D_2O characteristic peaks. This result indicates that the technical approach is reasonable, however improvement from sample preparation and reaction cell structure are in need. There are four possible approaches to improve the operando Raman reaction experiment.

First, we can acquire less dense (~15% porosity) $LiAlO_2$ pellet instead of standard pellets (~98% dense) to provide the more porous surface sample slice. This can promote more diffusion of wet gas within the sample surface.

Second, the microheater can be improved to achieve higher temperatures (~400°C) and more durability by using a reinforced structure and thicker heating materials (e.g., titanium and gold layers).

Third, the mixture of H_2O/ D_2O and N_2 gas can be applied using higher pressure in a reinforced reaction chamber, for example employing high pressure fittings (i.e., Swagelok parts). This should offer a higher efficiency of gas induction onto the pellet surface.

Forth, more Raman instrument time is needed. We had challenges in FY22 due to lack of instrument access (i.e., laboratory moving, instrument repairs). More testing time will allow improvement.

If we could implement the aforementioned improvements, it is anticipated that the isotopic exchange efficiency can be studied by changing the reaction chamber environment between N_2/H_2O and N_2/D_2O to quantify the isotope exchange rates using operando Raman spectroscopy while heating the pellet in a controlled manner.

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