Addressing Critical Problems in Materials Science Through Multiscale and Multimode Characterization (Project 1)

Characterization and Optimization of Novel Triple-Conducting Oxide Materials for Energy Applications (Project 2)

Cooperative Research and Development Final Report

CRADA Number: CRD-17-00711

NREL Technical Contacts: Mowafak Al-Jassim and Steve Harvey

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5K00-88980
February 2024

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NOTICE

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Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

Cooperative Research and Development Final Report

Report Date: February 21, 2024

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Colorado School of Mines (CSM)

CRADA Number: CRD-17-00711

CRADA Title:

Original Agreement Title: Addressing Critical Problems in Materials Science Through Multiscale and Multimode Characterization (Project 1)

Modification 1 Title: Characterization and Optimization of Novel Triple-Conducting Oxide Materials for Energy Applications (Project 2)

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Sponsoring DOE Program Office(s):

Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen Fuel Cell Technologies Office (HFCT)

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$80,000.00
Year 2	$80,000.00
Year 3	$40,000.00
Year 4, Modification #1	$0.00
TOTALS	$200,000.00

Executive Summary of CRADA Work:

Original Agreement:

Address critical problems in materials science and simultaneously advance the state-of-the-art in multiscale and multimode characterization using the combined advanced analytical capabilities and expertise of Colorado School of Mines (CSM) and the National Renewable Energy Laboratory (NREL). The primary effort of the Phase I of this CRADA is to establish the International Center for Multiscale Characterization using shared resources at both NREL and CSM. Phase II will focus on capability development and marketing, choosing candidate materials science issues in the areas of structure imaging, chemical composition mapping, and correlating properties and performance of materials for impact in energy-related, environmental and critical materials areas. The CRADA will be modified to include specific topics of concern in materials science to industry member partners.

Advanced analytical capabilities and expertise at CSM and NREL will be used to advance materials understanding and performance through characterization of multiscale phenomena including structural imaging, chemical composition mapping, and other techniques correlating properties and performance of materials.

Modification #1:

As part of the International Center for Materials Characterization, work under Modification #1 will be led by Colorado School of Mines (CSM), working in collaboration with NREL staff to mentor and advise CSM postdoctoral researchers on set up of diffusion annealing experiments.

The purpose of the modification is to provide for NREL staff to mentor and advise CSM postdoctoral researchers on set up of diffusion annealing experiments, including mentoring and advising the CSM-NREL team on proper Secondary Ion Mass Spectrometry (SIMS) data analysis as needed. SIMS measurements of 10-20 samples will be performed at NREL during the project duration.

CRADA benefit to DOE, Participant, and US Taxpayer:

- Assists laboratory in achieving programmatic scope,
- Adds new capability to the laboratory's core competencies,
- Enhances the laboratory's core competencies,
- Uses the laboratory's core competencies, and/or
- Enhances US. competitiveness by utilizing DOE developed intellectual property and/or capabilities.

Summary of Research Results:

ORIGINAL AGREEMENT

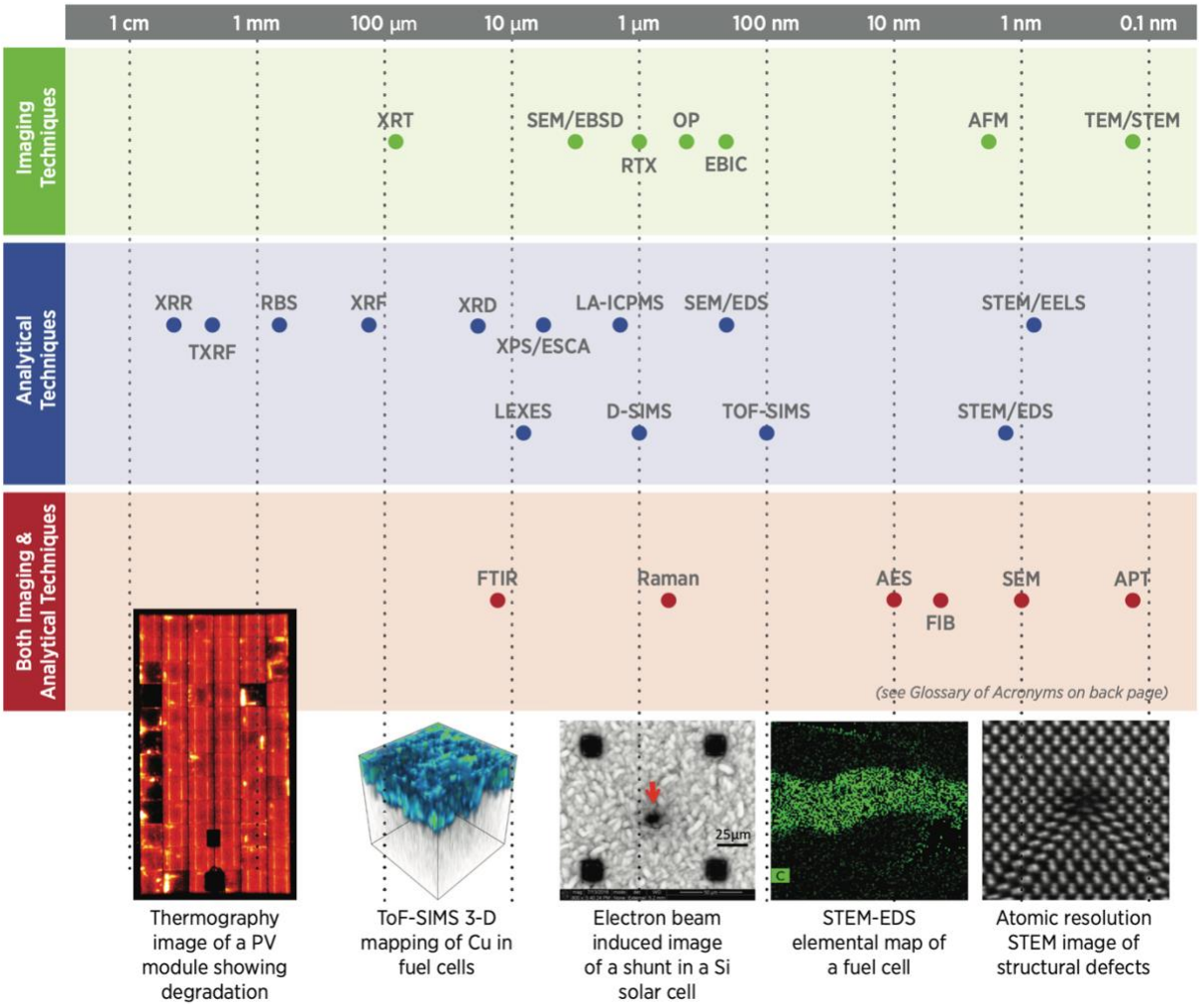
Summary of Original Agreement Research Results:

Task 1 (Phase 1): Establish International Center for Multiscale Characterization

Joining CSM and NREL's leadership capabilities in multiscale characterization, thought leaders will establish the guidelines, protocols, methods and bylaws for the ICMC, identify areas of interest and impact and provide staff to deliver the plans over the next three years. Create and review marketing materials, including a brochure, website, and presentations.

This task was accomplished by first surveying the characterization capabilities at both NREL and CSM. Special emphasis was placed on capabilities that are applicable to a wide variety of material classes. Additionally, techniques that cover length scales from meters to Angstroms were considered essential for this approach. The selected techniques included: optical microscopy, scanning electron microscopy, transmission electron microscopy, x-ray diffraction techniques, defect imaging techniques, such as photoluminescence, surface analysis techniques (Auger, XPS and SIMS) and chemical analysis techniques such as atom probe tomography, XRF and ICP-MS. Several areas of interest and impact were identified. These encompassed solar materials, battery materials, ceramics and metal alloys. Once the above was established, marketing materials were created. A brochure and a website detailing the combined NREL/CSM characterization capabilities were designed and circulated. Further, a presentation showing the capabilities and how they can be applied to solve important material problems was put together and was given in several places, such as Coors Tek, Lockheed Martin and CSM's open house.

An example of our marketing material (lifted from our brochure) is shown below. It illustrates the broad length scale (Angstrom to cm) and the powerful array of characterization capabilities offered.



Task 2 (Phase 2): Capability Demonstration

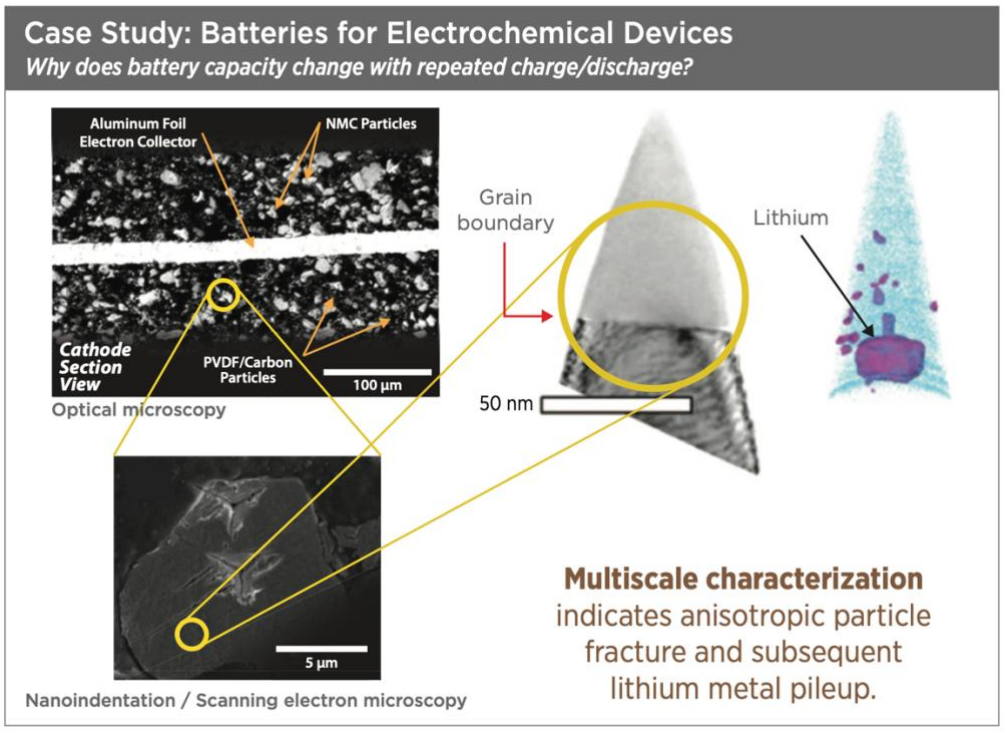
Demonstrate the applicability of the proposed multi-scale characterization approach to a wide variety of material systems. The latter includes, but is not limited to, fuel cells, battery electrodes, ceramics, metal alloys and dielectrics. Demonstrate the utility of multi-mode characterization in solving critical material science problems and develop/test new internal capabilities as needed. Specific topics of concern in materials science to industry member partners will be added to the scope of the CRADA to provide real-world demonstration of capabilities.

We demonstrated the applicability of the proposed multi-scale characterization approach to a wide variety of material systems and showed how such a powerful approach can solve important materials problems.

Below are two examples to illustrate that.

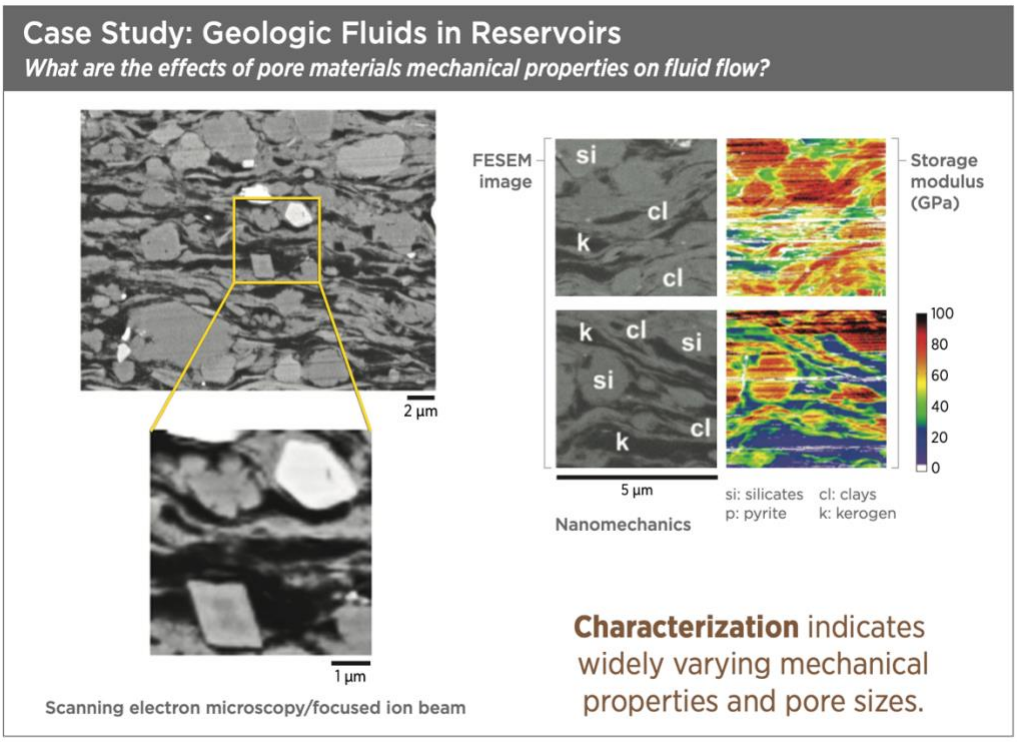
Example 1: Investigating battery capacity change

One of the critical issues in electrochemical storage is capacity change in lithium ion batteries. This was investigated by optical microscopy on the cm scale to study the morphology of the electrodes as they are cycled. Specific areas in the cathodes were selected for further investigations by scanning electron microcopy on the micron scale. Subsequently, sections of the cathode were lifted out by focused ion beam milling for nanoscale crystallographic investigation by transmission electron microscopy and chemical investigation by atom probe topography. The former indicated that there is a crystallographically preferred direction for fracture, leading to parts of the cathode being mechanically separated from the lithium conduction network; the latter showed that there is significant lithium ion pile up at grain boundaries. Having these combined results indicated both mechanical and chemical sources for the observed capacity decrease.



Example 2: Investigating geologic minerals in reservoirs

The effect of material porosity on fluid flow was investigated first by optical microscopy. Then specific areas were interrogated by high resolution scanning electron microcopy. SEM-based elemental mapping proved to be exceptionally valuable. The combination of high-resolution morphology studies of the material porosity and elemental mapping proved very valuable in understanding how the mechanical properties affect the fluid flow.



Task 3 (Phase 3): Identification and Characterization of Candidate Multiscale Phenomena

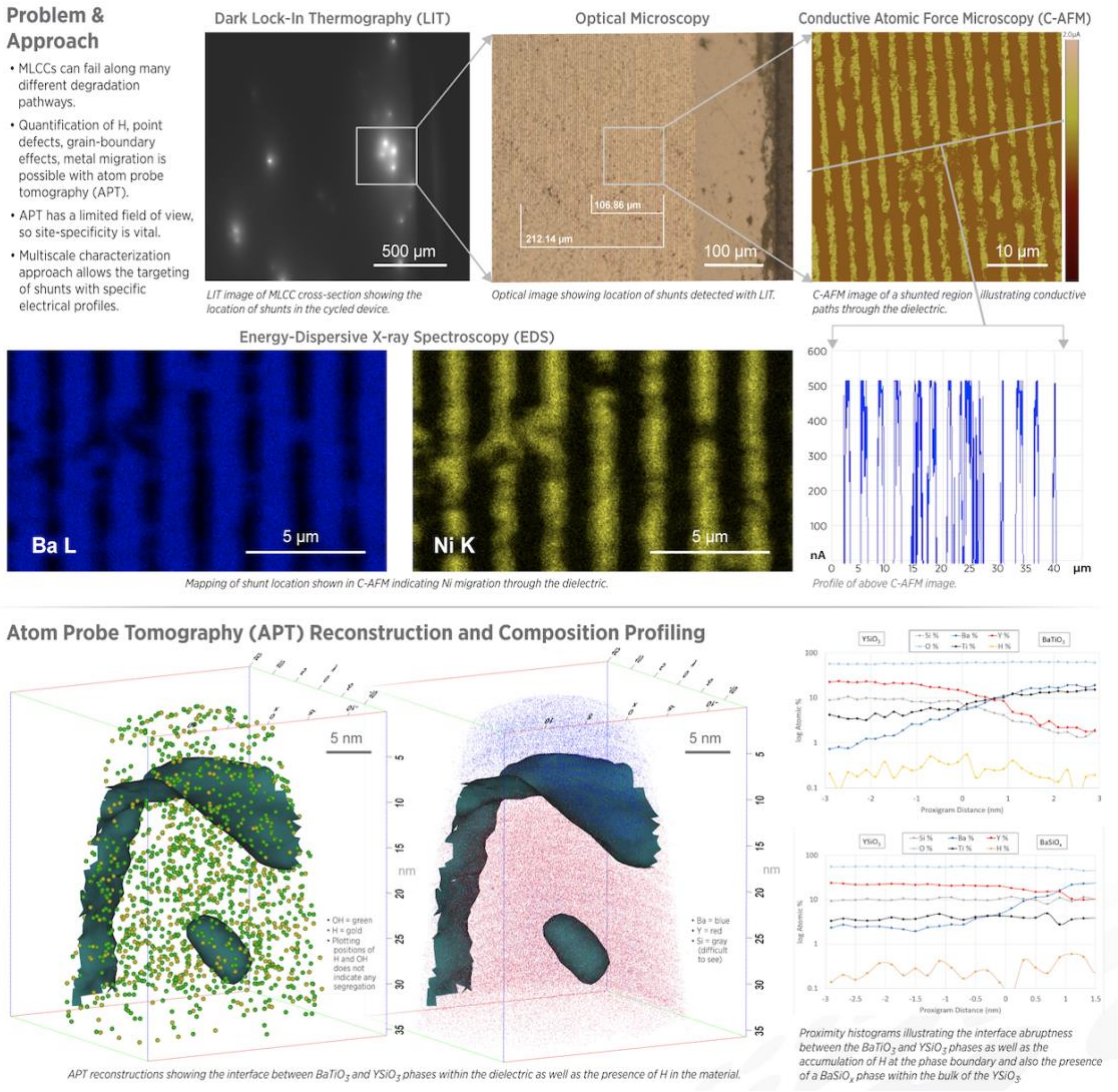
Establish close collaborations with local and national industrial partners and make presentations of ICMC capabilities and expertise. Test the applicability of multi-scale, multi-parameter characterization to advancing material properties and improving device performance. Develop understanding of potential industrial partner needs and impact areas in energy-related materials. Specific topics of concern in materials science to industry member partners will be added to the scope of the CRADA to provide real-world demonstration of capabilities.

We established close collaborations with local and national industrial partners and jointly explored important material problems with complementary multi-scale characterization techniques. Further, we made numerous presentations of ICMC capabilities and expertise to prospective collaborators. The latter included SolidPower Battery, CoorsTek, Ball Aerospace, Lockheed Martin, Newmont Mining and The Aerospace Corporation. In several of those interactions a wide range of problems were considered, and a few material issues were down-selected for preliminary investigations. Below is an example to illustrate this modus operandi.

Example: Investigating failure mechanisms MLCCs in collaboration with Aerospace Corporation

Base metal electrode (BME) multi-layer ceramic capacitors (MLCCs) are of growing interest for space applications due to benefits in form factor and performance compared to precious metal electrode (PME) devices. BME MLCCs can provide higher capacitance with decreased device volume. The lower weight, combined with a decrease in system complexity associated with the capacitance-voltage (C-V) characteristics of these devices, can result in significant cost reductions. However, space applications also demand high reliability and rigorous and established methods for qualification. While industry and government partners have invested in developing screening criteria and understanding failure modes under various operating conditions, less effort has gone toward investigating the physical mechanisms and performing the high-resolution, multimodal characterization required to fully model and ultimately eliminate the failure mechanisms.

In our preliminary work, we have demonstrated the ability to use lock-in thermography (LIT) to identify points of device failure and then mark those locations to provide site-specific characterization using scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDX) for physical and chemical imaging, conductive atomic force microscopy (AFM) for local electrical property variation mapping, and atom probe tomography (APT) and secondary ion mass spectrometry (SIMS) for high resolution chemical mapping and reconstruction. This powerful combination of capabilities, along with the expertise to correlate points of failure from the macroscopic to the atomic level, could potentially offer a breakthrough opportunity to understand, address, and reduce failure modes for these important devices for next-generation space systems.



MODIFICATION 1

Summary of Modification #1 Research Results:

The CRADA was setup as a framework agreement for the International Center for Materials Characterization (ICMC), which was a joint effort between CSM and NREL to provide advanced characterization to industrial partners. The ICMC was a joint effort internally funded by CSM and NREL for 3 years to try to get off the ground. Unfortunately, the center generated a lot of interest but did not land a significant agreement with any prospective partners and the ICMC work stopped when the internal support ended.

Task 1: Set up of Diffusion Annealing Experiments

Existing equipment in the CSM lab will be modified and combined to be suitable for tracer gas diffusion annealing experiments. A mass spectrometer will be connected to the small, closed volume quartz furnace tubing to measure 18O2 gas (purified oxygen) content in the gas phase before and after diffusion annealing experiments are performed, which will allow for the appropriate inputs to the diffusion solution to be measured. A second setup for deuterium gas will be made with alumina tubing and a heavy water bubbler, and the samples will be exposed to a flowing atmosphere of deuterium containing water vapor. Both experiments will create samples with a diffusion profile of the tracer elements, $^{18}O_2$ and deuterium.

In the first three months, samples will be prepared and polished so they are most suitable for SIMS diffusion profile measurements. The experimental setup in the CSM lab will be modified to be suitable for tracer gas diffusion experiments. SIMS measurements and analysis will be completed on initial samples, and iterations on the experimental conditions will be made to allow for diffusion profiles within a 1-3 micron length from the sample surface, if possible.

The CRADA mod 1 was initiated as an incubator to start oxygen and deuterium diffusion studies on solid oxide fuel cell materials being developed at CSM, the funds in to NREL were only to support TOF-SIMS measurements of the samples as well as support to act as in an advisory role for the diffusion experiments as CSM was new to this area. The amount of money transferred was quite small (15K), but since the ICMC CRADA already existed and the work fit the scope, the ICMC CRADA was used as a first test case of this CRADA to transfer funds easily between NREL and CSM.

The partners at CSM for Mod 1 initially modified and combined existing equipment in the CSM lab to be suitable for tracer gas diffusion annealing experiments as shown in Figure XYY. A mass spectrometer was connected to the small, closed volume quartz furnace tubing to measure $^{18}O_2$ gas (purified oxygen) content in the gas phase before and after diffusion annealing experiments were performed, which allowed for the appropriate inputs to the diffusion solution to be measured. The experiments created samples with a diffusion profile of the tracer elements, $^{18}O_2$. Due to the initial difficulties encountered with the 18O2 tracer diffusion experiments, the work on Deuterium was postponed and carried out after conclusion of the CRADA.

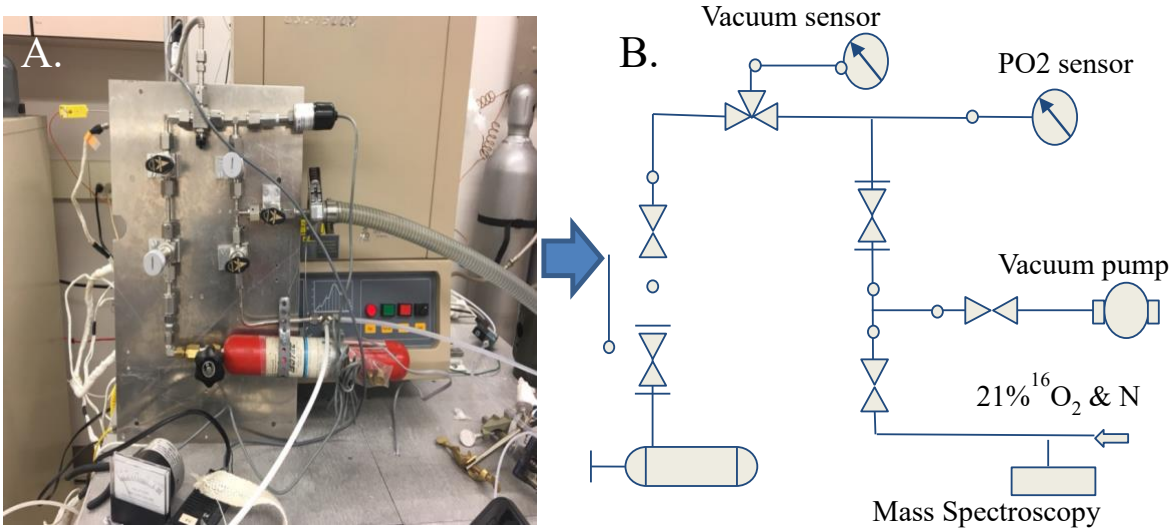


Figure XYY: A) photo of the modifications made on the isotope exchange setup at CSM as part of task 1. B) schematic of the system shown in A.

Task 2: SIMS Measurements and Data Analysis

NREL will obtain samples from the staff at CSM and perform SIMS measurements on the tracer diffusion samples, as well as provide feedback to guide the experimental conditions. Since the diffusion coefficient of $^{18}O_2$ in a new composition is not known, it's likely that the first diffusion profiles may be far too shallow to the surface or even far too deep into the sample. Since four TCO compositions at a fixed temperature are planned to try to gain some insight into how cation ratios affect the transport, it is likely the experimental conditions will need to be iterated a few times for each composition until high-quality data is collected.

NREL will provide the SIMS data to CSM and advise and assist the CSM post-doc who is currently working on TCO (triple-conducting oxide) materials for CSM on proper data analysis for the relevant diffusion conditions of the experiments.

Timeline for Task 2: In months 6-12 a scope of work within the limited budget to look at oxygen and deuterium diffusion in four different TCO compositions at one fixed temperature is planned. This will give CSM some insight into the relationship that cation substitution has on the transport properties. If additional time and budget allows when the work on these initial compositions finishes, the scope could potentially be expanded to investigate either more material compositions, or even explore the temperature dependence of diffusion in one or more TCO compositions. In months 6-12 these preliminary data may be used in a proposal to other funding agencies with a much larger scope of work in mind for future efforts performed under an additional modification to this agreement.

Task 2 involved the SIMS measurement of the diffusion samples. The initial samples were polished and subjected to a diffusion anneal for SIMS diffusion profile measurements. Initial SIMS measurements revealed very long diffusion profiles, so the samples were sectioned and polished to do SIMS maps of the pellet cross section. Issues with sample preparation due to sample curvature introduced during cross-sectional polishing led to artifacts in the SIMS data, as shown in Figure XX. Advice for better sample preparation was given and the sample polishing was further optimized by imbedding the sample cross section in a polymer resin and then polished, which led to suitable quality SIMS line scans of the $^{18}O_2$ tracer diffusion profiles as shown in Figure XY. Since both the surface exchange coefficient and the diffusion coefficient of the material was unknown, it took many iterations of diffusion time and temperature to find conditions which lead to a diffusion profile above the natural abundance background for $^{18}O_2$ (0.2%) and with a sufficient depth within the sample to yield a good profile shape which could be accurately fit to the appropriate diffusion solution. At least 20 SIMS profiles were taken on control and diffusion-exchanged samples to obtain these data. One example diffusion anneal profile is shown in Figure XZ, where the SIMS data were provided to CSM and the suggestions for iterations on the anneal conditions were made until the activation energy for diffusion and the surface exchange coefficient were determined as 58.99 ± 0.447 (kJ/mol) for D and 72.63 ± 0.67 (kJ/mol) for k, the Arrhenius plots for which are shown in figure YYX. The values for the surface exchange coefficient and diffusion coefficient were determined.

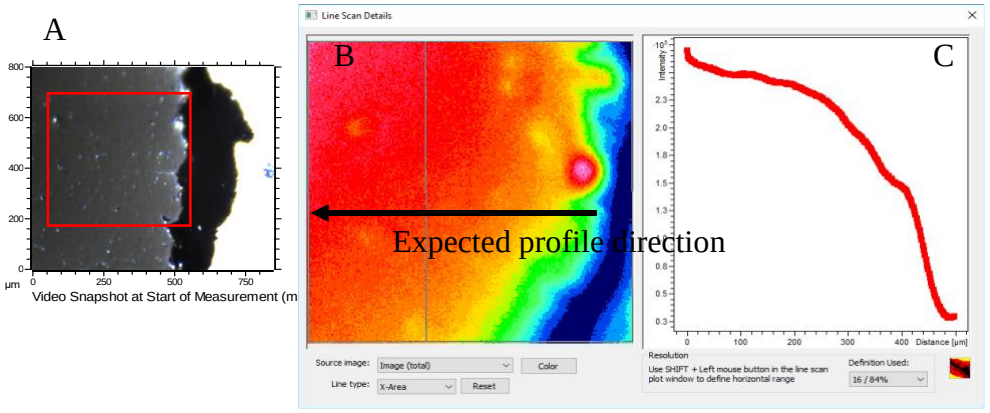


Figure XX: shows issues with initial sample preparation on the SIMS data. A) optical image of the pellet cross section, where the red square shows the approximate 500x500µm analysis area. B) The total ion counts image of the analysis area, where red means higher counts and blue lower counts, a large fall off in counts is seen near the pellet edge. C). The line-scan across the dataset shows that the sample preparation artifacts mask any potential diffusion profile in the data.

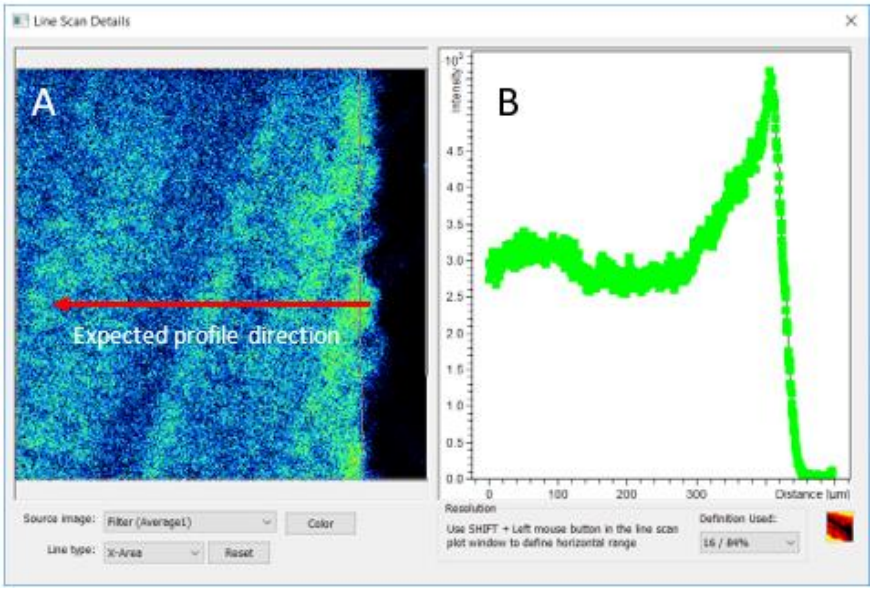


Figure XY: A) TOF-SIMS image of the 18O SIMS signal of a pellet cross section after the 18O2 diffusion anneal, the ideal sample prep led to much better data quality. B). The SIMS linescan of the 18O image data shown in A, the diffusion direction is from right to left in the image, after the initial rise in signal where the pellet is reached, a diffusion profile is seen in the 300–400-micron range before the background levels for 18O are reached.

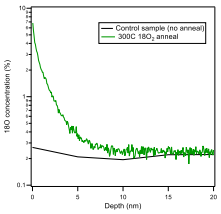


Figure XZ: 18O concentration showing the diffusion profile of a sample annealed at 300C for 1 hour in 18O2 gas.

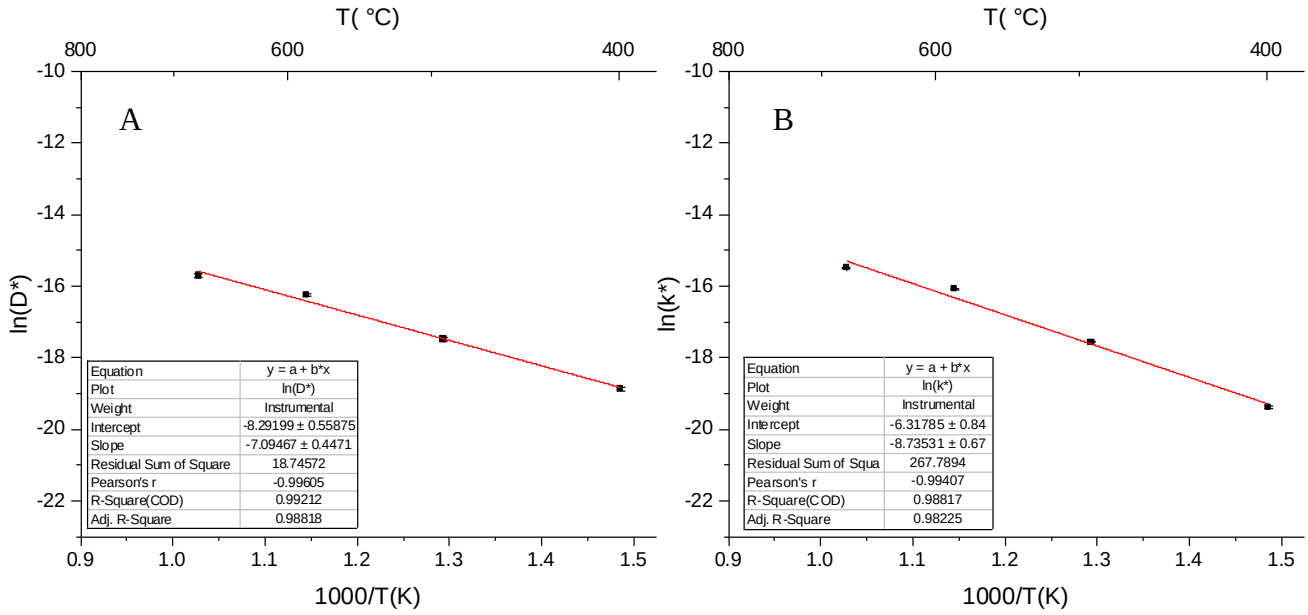


Figure YYX: Arrhenius plots for A) The oxygen diffusion coefficient (D) and B) The surface exchange coefficient (k) for the BCFZY4411 material.

About halfway through the period of performance (PoP) for Mod 1 CSM acquired a state-of-the-art TOF-SIMS V instrument, shortly after that, CSM started to work directly with their own TOF-SIMS and phased out the interaction with NREL on this project. The scope of work initially included looking at more compositions with the TOF-SIMS at NREL, but due to this new development this work was completed at CSM instead, and about half of the Mod1 agreement ended up unspent and was returned to CSM.

Subject Inventions Listing:

None.

ROI #:

None.