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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Northeastern University
360 Huntington Avenue
490 RP
Boston, MA 02115 -5005

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UU	UU	UU	UU		19b. TELEPHONE NUMBER 617-373-7526

RPPR Final Report
as of 27-Dec-2018

Agency Code:

Proposal Number: 71943CHII **Agreement Number: W911NF-17-1-0557**
INVESTIGATOR(S):

Name: Eugene Smotkin
Email: e.smotkin@neu.edu
Phone Number: 6173737526
Principal: Y

Organization: **Northeastern University**
Address: 360 Huntington Avenue, Boston, MA 021155005
Country: USA
DUNS Number: 001423631 EIN: 104167998
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Submitted By: Eugene Smotkin Email: e.smotkin@neu.edu
Phone: (617) 373-7526
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STEM Degrees: 2 **STEM Participants:** 3

Major Goals: This final report describes work towards development of operando Raman spectroscopic methods for characterization of intermediate temperature (500-650°C) mixed ionic-electronic conducting (MIEC) oxide membranes for air separation. The proposal aims were to (1) develop procedures for preparation of MIECs for oxygen separation, and (2) to develop operando Raman spectroscopic methodologies applicable to hot MIEC membranes beneath a CaF2 window. A consideration related to Raman micro-spectroscopy of hot surfaces is the distance required between the microscope objective and the hot oxide surface. In addition to this, the in-house procedure for making mixed fluorite-perovskite disks was established.

Accomplishments: 1. A new method of Raman micro-spectroscopy was developed. The technique, Defocused Confocal Raman Micro-Spectroscopy (DCRMS) enables the collection of Raman photons outside of the laser focal point to avoid photoablation.

2. The hardware required to cast "green layers" of perovskite/fluorite mixed ionic electronic conductors was developed.

3. A ball milling procedure for preparation of the MIEC was confirmed by Raman Spectroscopy and XRD.

4. Future work was proposed which includes oxygen separation and the use of proton conducting oxides for high temperature chemical transistors.

Training Opportunities: The participants included 2 graduate students, one undergraduate and one professional staff member. Two manuscripts were produced. One is published and the other revised as per editor of Journal of Chemical Physics.

RPPR Final Report
as of 27-Dec-2018

Results Dissemination: 1. Loupe, N.; Doan, J.; Cruse, R.; DiMarzio, C. A.; Smotkin, E. S., Laser focal point sequestration for Raman micro-spectroscopy of thermally sensitive fuel cell catalytic layers. Electrochim. Acta 2018, 283, 1079-1086.

2. Dimakis, N.; Salas, I.; Gonzalez, L.; Loupe, N. and Smotkin, ES, Electron Density Topological and Adsorbate Orbital Analyses of Water and Carbon Monoxide Co-adsorption on Platinum, Journal of Chemical Physics, AIP, Submission # A18.06.0233R1 Final revisions submitted Dec. 3, 2018

3. PhD Dissertation by Neili Loupe

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Staff Scientist (doctoral level)
Participant: Jon Doan
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Nestor E Navarro
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Neili Loupe
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Ryan O'Hagan Mr
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

RPPR Final Report
as of 27-Dec-2018

Final Report
Short-Term Innovative Research (STIR) Program

Operando micro-Raman spectroscopy: Intermediate temperature MIEC air-separation membranes

W911NF-17-1-0557

Northeastern University
Organization's Unique Entity Identifier: 001423631
Eugene S. Smotkin

Abstract: This final report describes work towards development of operando Raman spectroscopic methods for characterization of intermediate temperature (500-650°C) mixed ionic-electronic conducting (MIEC) oxide membranes for air separation. The proposal aims were to (1) develop procedures for preparation of MIECs for oxygen separation, and (2) to develop operando Raman spectroscopic methodologies applicable to hot MIEC membranes beneath a CaF_2 window. A consideration related to Raman micro-spectroscopy of hot surfaces is the distance required between the microscope objective and the hot oxide surface. In addition to this, the in-house procedure for making mixed fluorite-perovskite disks was established.

Raman micro-spectroscopy with a sequestered focal point

Raman micro-spectroscopists examining historical art were first to work out of focus. They worked with the laser focal point above the sample and acquired Raman photons from below the waist of the beam. This eliminated photoablation of the art work at the focal point. This methodology was never a broadly used technique because the theory behind defocused micro-spectroscopy was never well developed. Defocused micro-spectroscopy is still a confocal method (i.e., The laser focal point is conjugate to the detector pin-hole). Further, prior to this STIR work, no consideration was given to Raman photons generated at a focal point distant from the sampling region of interest. These photons are background noise that must be dealt with. This component of the report discusses the theory of the defocused confocal Raman micro-spectroscopy (DCRMS). Figure 1 places DCRMS in the context of the current practices.

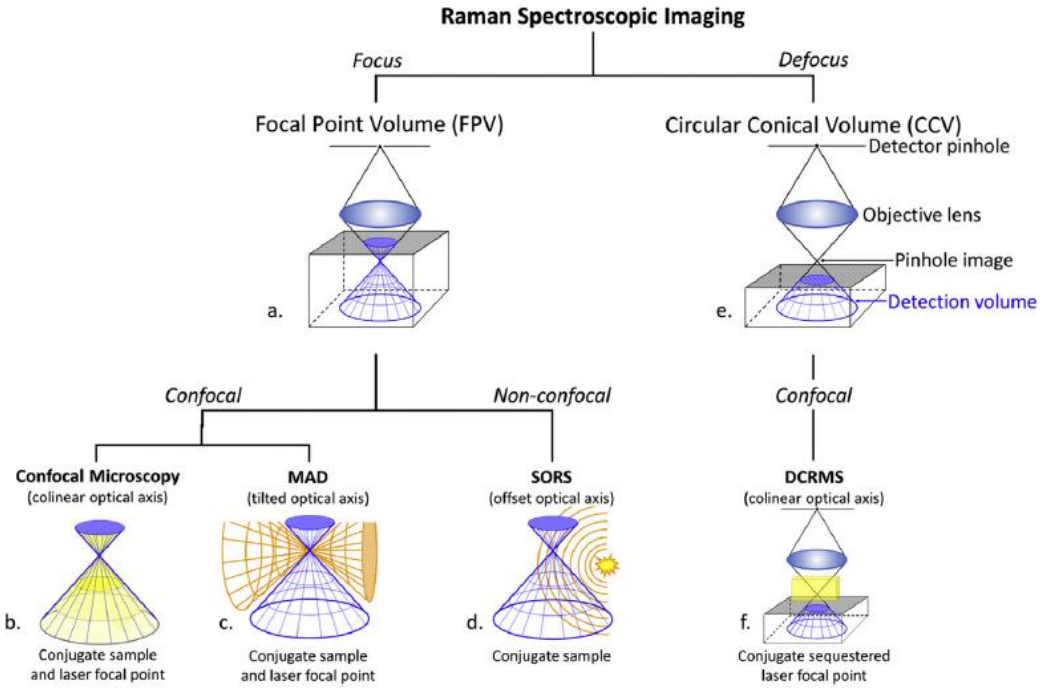

Figure 1. Raman micro-spectroscopy separated between focused and defocused modes.

Microscopic imaging is performed almost exclusively in focus (Fig. 1a. – d.). Focused imaging, confocal (Fig. 1b.-c.) or non-confocal (Fig. 1d.), irrespective of the laser focal point position, detects Raman photons originating at the detector pinhole image. A method is confocal when the laser focal point is conjugate to the detector pinhole (Fig. 1b.-c.) If confocal imaging is done in focus, photoablation can occur (1).

There are few, but seminal reports of defocused confocal Raman micro-spectroscopy (DCRMS) where the laser focal point is conjugate to the detector pinhole yet outside the illuminated volume of interest (Fig. 1e). The DCRMS configuration was routinely used by McDonald and Vaughan [73] for analysis of historical art works. Photoablation was mitigated by positioning the focal point above the surface of the painting. In later work, Lin et al. [63] used DCRMS for the study oligonucleotides chemisorbed upon a gold surface. McDonald and Vaughan [74] revisited DCRMS with a finite element model. Figure 1f advances the methods theorized by McDonald by sequestering the focal point and thus eliminating the background. There are no Raman photons generated in the isotropic medium that overlap the sample bands of study.

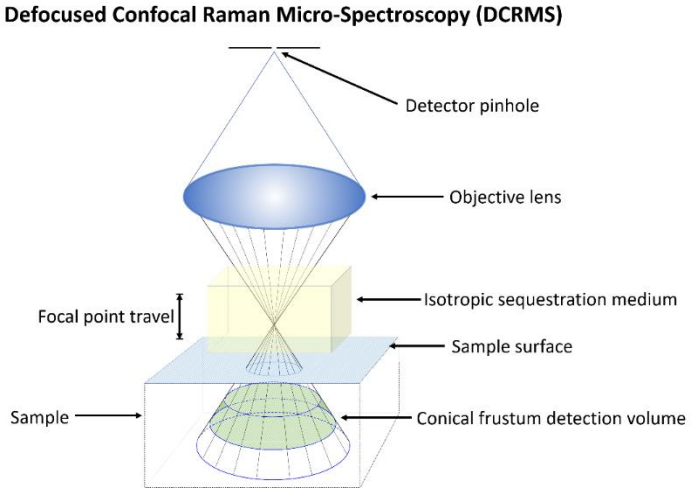

Figure 2 shows the details of focal point sequestration.

The focal point travel is entirely sequestered in an isotropic medium (yellow medium) that yields no Raman photons (i.e. CaF_2). This system was used to z-section an entire single cell fuel cell assembly. (2) Within the STIR program the theory of DCRMS, coupled with focal point sequestration, was fully developed. Details can be found in reference 2.

Figure 3 summarizes the advantage of sequestering the focal point. The average normalized solid angle within the sample (green), with surface 9 units below the focal cell, is ~1 % of that at the focal point. Upon sequestration of the focal point in an isotropic medium (i.e., free of Raman bands over the range relevant to the sample), the average normalized solid angle within the sample increases to ~13 % of that resulting from the unsequestered region (Fig. 3, dotted line).

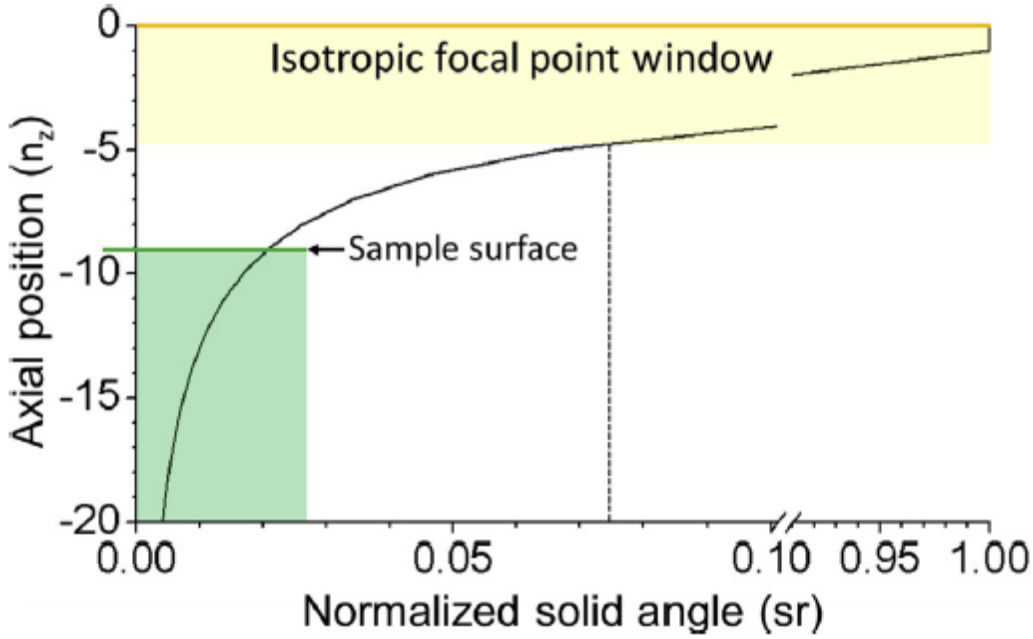

Figure 3. The 20-cell finite element simulated predicted signal per unit sample volume emanating from the axial cells based on geometrical constraints alone for a zero-extinction sample with a space filter established by an isotropic-focal-point-window (yellow) and resulting sampling region (green).

The DCRMS will enable acquisition of Raman spectra of a hot flow cell under development. The focal point will be sequestered using a microscope objective with a 7 mm working distance. This will enable comfortable travel of the laser focal point (for Z sectioning) from the hot surface.

Mixed ionic – electronic conducting oxides.

Preparation of MIEC

To prepare the mixed ionic-electronic conducting (MIEC) powder, 10.93 g of gadolinium-doped ceria (GDC) was mixed with 10.21 g of lanthanum stronium manganite (LSM) and ~100 g of 1mm yttrium-stabilized zirconium (YSZ) grinding beads. The homogenized powder was then slowly added to a beaker filled with 21 mL of isopropanol with 2 wt% of polyvinyl butyral and mixed thoroughly. The mixture was ball milled for a period of 24 h, before being sintered at a temperature range of 1000–1100 ◦C with a 4 h soak time in air.

A sample of the resulting powder was analyzed via x-ray diffraction (XRD) and compared with XRD scans of a homogenized 80:20 by vol. mixture of GDC and LSM. Upon observing adequate peak-shifting, it was confirmed that ball-milling had sufficiently blended the two oxides, and that the MIEC powder was formed (Fig. 4)

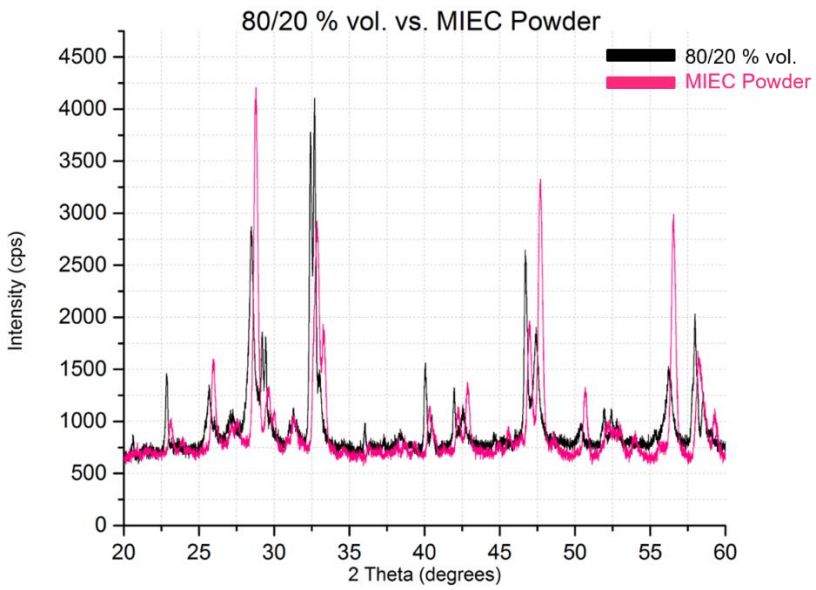

Fig. 4 XRD patterns of the MIEC powder were compared to those of an 80:20 by volume mixture of GDC and LSM. Peaks were shown to have retained approximate shape and intensity, but were shifted ~3°, indicating adequate interfacing.

A heated casting table was assembled for doctor blading of green layers of the MIEC (Fig. 5)

Fig. 5. The casting table has a heated casting surface for evaporation of solvent. The enclosure T is also controlled. The slurries are cast using the doctor blade (right side).

Our first Raman spectrum obtained of the fluorite-perovskite MIEC at room temperature is shown in Figure 6.

Raman breathing mode of perovskite A metal (ABO_3) octahedrally coordinated to 6 oxygen atoms.

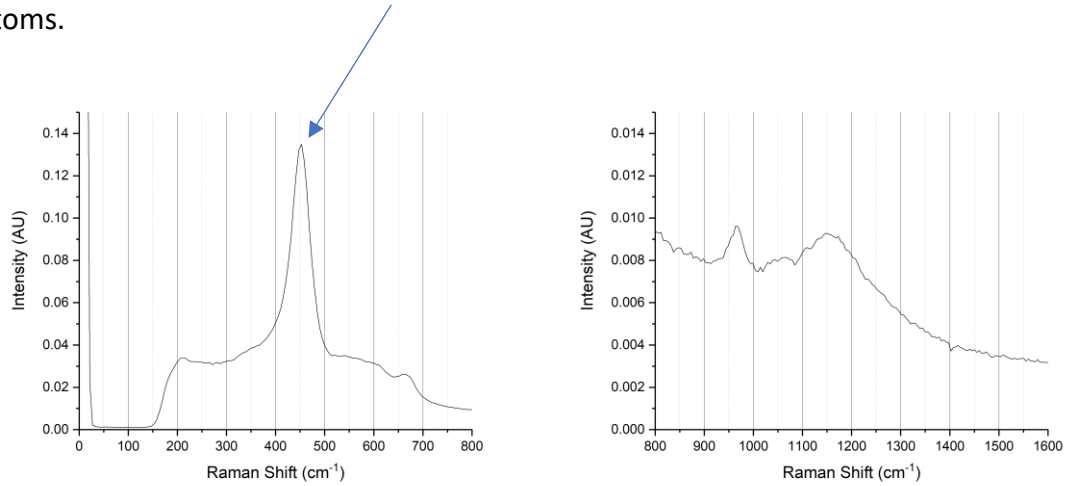

Fig. 6. Raman spectra of the GDC-LSM MIEC taken with sequestered focal point

Figure 7 (taken from proposal) shows the perovskite (a) and fluorite (b) unit cells. Fluorites are AO_2 structures: A is a tetravalent atom that occupies the corner and faces of a face centered cubic cell. Each corner atom contributes to a tetrahedral void that includes the three nearest neighbor face centered atoms. All tetrahedral voids are occupied by an oxygen atom (red). Accepter dopants such as Gd^{3+} or Sm^{3+} introduce oxide vacancies, which are required for oxide mobility. As mentioned in the proposal, the 8 oxygen atoms coordinated to one metal atom (Fig. 7a) gives rise to the Raman breathing mode at 460 cm^{-1} (Fig. 6 left). This peak is observed in our preliminary spectroscopy (Fig. 6 left). Accepter dopants and/or interaction with a neighboring phase of perovskites will shift of broaden the 460 cm^{-1} band.

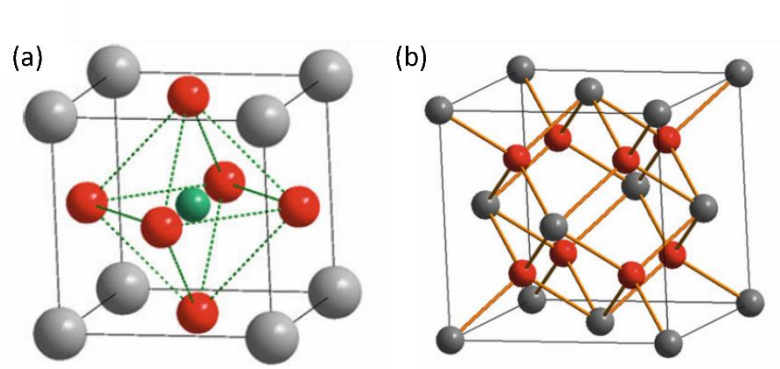

Figure 7. Perovskite and fluorite unit cells: oxygen atoms red; (a) ABO_3 perovskite structure: A atoms (grey); B atoms green. (b) CeO_2 fluorite unit cell; Ce^{4+} (gray). Adapted from Zhu et al.(3)

Future work

A substantial effort was expended at developing the theory of Defocused Confocal Raman Micro-spectroscopy and oxide membrane preparation. Future work involves:

1. Varying the blend of perovskite/fluorite MIEC and examining the shift and broadening of the 460 cm^{-1} breathing mode. This experimental work would be corroborated by quantum theory of atoms in molecules (QTAIM) and by adsorbate orbital approaches. Polyhedral structures such as MIEC structure are perfect subjects for electron density topological studies. Our paper (Dimakis et al., 2018) uses the method of Bader to visualize electron density topologies. This is a major shift from the concept of bonds as observables.

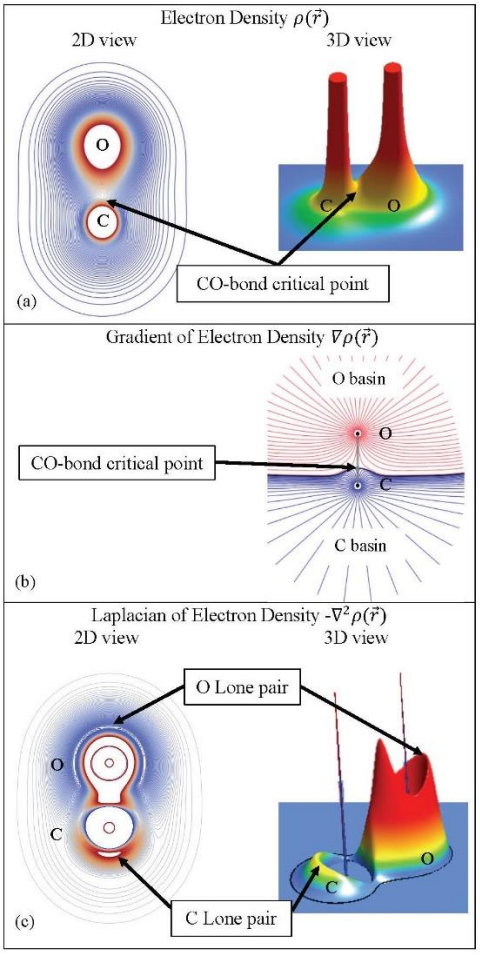

FIG. 8. (Taken from Dimakis, Smotkin et al. J. Chem. Phys., 2018 submitted). This figure introduces and electron density topological view versus the more commonly used bond views. This work was funded in part by the STIR program.

Figure 8 shows a molecular structure (CO) in terms of the electron density topology. In our future oxide work, we aim to represent electronic densities topologically as well as in

conventional orbital theory. interesting, and unprecedented to represent oxide MIECs in this format.

2. We are working on proton conduction perovskites to serve as cathodes for high temperature chemical transistors to effect isomerization of fully saturated hydrocarbons at below 400°C.

3. We will continue the work on intermediate temperature oxygen separation membranes using fluorite-perovskite membranes. The operando spectroscopy oxygen separation cell is under development.

Student effort: Students and staff funded (direct costs) by the STIR program are enumerated below.

1. Jon Doan, staff scientist: $1,320
2. Neili Loupe, Grad Student: $17,393 Graduated with PhD; December 2018
3. Nestor E. Navarro, Grad Student: $11,595
4. Ryan O'Hagan, Undergrad: $720

Publications (2)

1. Loupe, N.; Doan, J.; Cruse, R.; DiMarzio, C. A.; Smotkin, E. S., Laser focal point sequestration for Raman micro-spectroscopy of thermally sensitive fuel cell catalytic layers. *Electrochim. Acta* **2018,** *283*, 1079-1086.

2. Dimakis, N.; Salas, I.; Gonzalez, L.; Loupe, N. and Smotkin, ES, Electron Density Topological and Adsorbate Orbital Analyses of Water and Carbon Monoxide Co-adsorption on Platinum, Journal of Chemical Physics, AIP, Submission # A18.06.0233R1 Final revisions submitted Dec. 3, 2018

Patents

Request for provisional patent submission to Northeastern IP office.

Final report references

1. Lin X-M, Cui Y, Xu Y-H, Ren B, Tian Z-Q. Surface-enhanced Raman spectroscopy: substrate-related issues. Analytical and bioanalytical chemistry. 2009;394(7):1729-45.
2. Loupe N, Doan J, Cruse R, DiMarzio CA, Smotkin ES. Laser focal point sequestration for Raman micro-spectroscopy of thermally sensitive fuel cell catalytic layers. Electrochim Acta. 2018;283:1079-86.
3. Zhu X, Yang W. Ionic Conductors and Aspects Related to High Temperature. In: Zhu X, Yang W, editors. Mixed Conducting Ceramic Membranes: Fundamentals, Materials and Applications. Berlin, Heidelberg: Springer Berlin Heidelberg; 2017. p. 49-93.