Experiment Proposal

Experiment number GP2023024

Principal investigator (*)	Dr Marcello Marelli, CNR, ITALY
Co-investigator Co-investigator Co-investigator Co-investigator Co-investigator Co-investigator Co-investigator Co-investigator	Mr Andrea Strazzolini, University of Udine, ITALY
Experiment title	Disclose Exsolved double perovskite SFMN nanostructure

MRF Instrument	**High Resolution TEM**	**Days requested:** 3	
Access Route	Direct Access	**Previous GP Number:** -	
Science Areas	Chemistry, Energy, Materials	**DOI:** -	
Sponsored Grant	Yes	**Sponsor:** Other	
Grant Title	Contratto per TEM, UNIUD,CNR-SCITEC	**Grant Number:** -	

Start Date	16/11/2021	**Finish Date:** -
Similar Submission?	-	
Industrial Links	-	

Non-Technical Abstract

In the last decade, double perovskite (A2BB′O6) oxides are an alternative to cermet SOC electrodes, due to the possibility of easily tuning their electronic-ionic conductivity and catalytic properties by doping A and B sites with aliovalent ions and by their exsolution from the perovskite structure. Strontium-molybdenum-double perovskites (SMMoO6, with M=Mg, Ti, Ni, Fe) have recently found great application as anode and cathode in SOC. They show a high electronic and oxygen ion conductive, considerable resistance to carbon and sulfur poisoning and a good redox thermal and mechanical stability. We want to exploit the structural changes of Sr2FeMo0.6Ni0.4O6-δ after the exsolution process. We want to use HRTEM and EDS-MAPS analysis to disclose those peculiar structures and to collect imaging at high-resolution to extract crystalline information next to morphological arrangements.

Publications

ISIS neutron and muon source

IM@IT E-platform: No

Instruments	**Days Requested:**
Access Route	**Previous RB Number:**
Science Areas	**DOI:**
Sponsored Grant	**Sponsor:**
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ISIS@MACH ITALIA

Science and Technology Facilities Council
ISIS Neutron and Muon Source

Sample record sheet

Principal contact	Dr Marcello Marelli, CNR, ITALY		
MRF Instrument	**High Resolution TEM**	**Days Requested:** 3	
Special requirements:			

SAMPLE

Material	SFMN exsolved system 1 Low temperature	SFMN exsolved system 2 intermediate temperature	SFMN exsolved system 3 High temperature
Formula	Sr2FeMo0.6Ni0.4O6-δ	Sr2FeMo0.6Ni0.4O6-δ	Sr2FeMo0.6Ni0.4O6-δ
Forms	Friable powder	Friable powder	Friable powder
Volume	cc	cc	cc
Weight	10 mg	10 mg	10 mg
Container or substrate	The sample will be prapared onto a lacey-Carbon film TEM Cu Grid	The sample will be prapared onto a lacey-Carbon film TEM Cu Grid	The sample will be prapared onto a lacey-Carbon film TEM Cu Grid
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	- K	- K	-
Pressure Range	- mbar	- mbar	- mbar
Magnetic field range	- T	- T	-
Standard equipment	None	None	None
Special equipment	N/A	N/A	N/A

SAFETY

Prep lab needed	No	No	No
Sample Prep Hazards	NO	NO	NO
Special equip. reqs	NO	NO	NO
Sensitivity to air	No	No	No
Sensitivity to vapour	No	No	No
Experiment Hazards	NO	NO	NO
Equipment Hazards	-	-	-
Biological hazards	NO	NO	NO
Radioactive Hazards	NO	NO	NO
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Returned to user by instrument scientist (when inactive)	Returned to user by instrument scientist (when inactive)	Returned to user by instrument scientist (when inactive)

Science Case -Disclose Exsolved double perovskite SFMN nanostructure – Dr. Marcello Marelli CNR-SCITEC Milano

1. Background and Context

In the context of developing a circular economy for greater sustainability of human activities, it is vital to develop technologies for low-cost and low-environmental-impact conversion of energy from renewable sources. Solid oxide cells (SOCs) are nowadays one of the most promising energy conversion technologies, to accelerate and promote the ongoing energy transition based on the use of renewable resources. These devices in fact allow the creation of valuable low-carbon footprint power-to-X (X= power, fuels) chains of energy conversion and storage. It is crucial to design innovative materials and processes for more versatile and reversible devices.

In the last decade, double perovskite ($A_2BB'O_6$) oxides have been proven to be a valuable alternative to cermet SOC (Solid oxide cells) electrodes, due to the possibility to easily tune their electronic-ionic conductivity and catalytic properties, as by doping A and B site with aliovalent ions or changing their stoichiometry and structure. Among these approaches, the exsolution of metal dopants from the perovskite lattice has been gaining popularity as an effective way to increment and stabilize SOC electrodes. However, the exsolution process (both by thermal reduction or electrochemical cathodic polarization) still lacks a comprehensive rationalization, as it is strongly dependent on the specific type of metal and perovskite studied. Strontium-molybdenum-double perovskites ($SMMoO_6$, with M=Mg, Ti, Ni, Fe) have recently found great application as anode and cathode in solid oxide cells,(SOC) since they show generally a high electronic and oxygen ion conductive, considerable resistance to carbon and sulfur poisoning and a good redox thermal and mechanical stability. As regards Ni-doped Sr_2FeMoO_6 perovskites, their thermal reduction at a temperature at least of 800°C leads to a multiphase system consisting of a Ruddlesden-Popper phase (RP phase), a perovskite-like phase and Ni-Fe alloy particles embedded in the perovskite matrix. In this work, we want to explore the structural changes of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ (SFMN) systems after the exsolution process, obtained following different exsolution' procedures and redox treatment. This process leads to radical local compositional changes and enrichment in the crystal complexity at the nanoscale. A deep understanding of the local nanostructure of these materials and their relation with their own bulk activity is pivotal to optimizing the synthesis and the enabling processes, and investigate other potential applications (chemical looping, catalytic processes). This project is framed in a more wide scientific collaboration between CNR-SCITEC (and in detail with Dr. Marcello Marelli, PI for this proposal) and Università di Udine about the advanced structural and morphological characterization of engineered perovskites systems for energy production. The proposal is supported by a dedicated grant and personal funding at CNR-SCITEC.

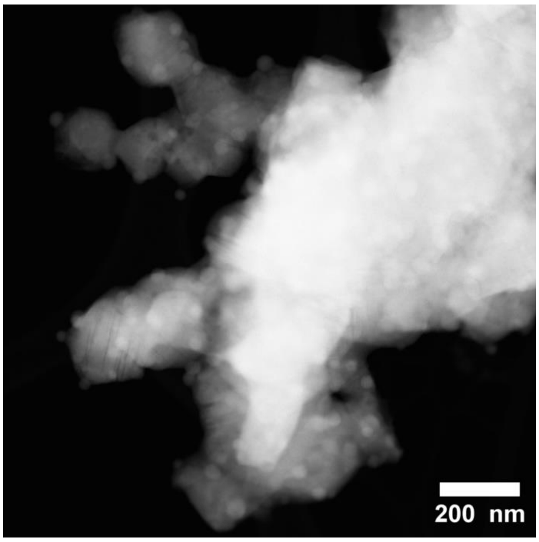
2. Proposed experiment

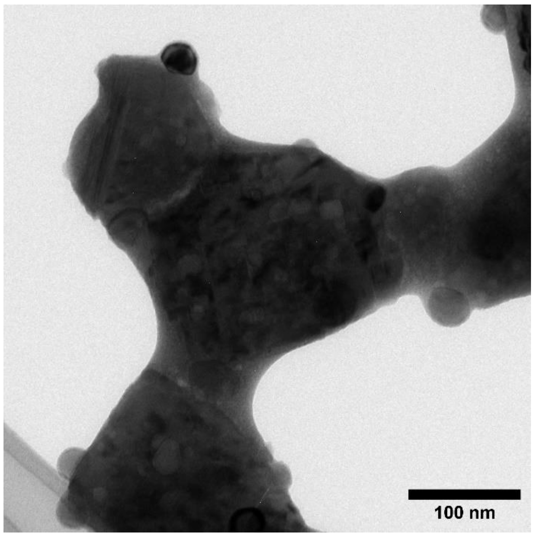
In this work, we want to exploit the structural changes of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ (SFMN) systems after the exsolution process, following different procedures. This process leads to radical local compositional changes and enrichment in the crystal complexity at the nanoscale. The key objectives for this proposal are to use HRTEM and EDS-MAPS analysis as unique tools able to disclose those peculiar structures retaining the spatial information. We want to collect imaging at high-resolution to extract crystal structure information next to morphological arrangements. Finally, elemental EDS MAPS will be primary to better understand the self-re-organization that crystal SFMN materials meet after thermal treatments. The sample batch is composed of three-four selected samples treated by different exsolution processes and related to interesting and promising activity results. Specimen will be prepared at CNR-SCITEC lab, using Lacey-carbon Copper TEM-grid, in accordance with general procedures shared with the ICCOM labs.

The TEM instrument available at ISIS@MAC ITALIA – the ThermoFisher Talos F200X –offer high performance energy dispersive x-ray spectroscopy (EDS) signal detection and 3D chemical characterization with compositional mapping. Fits very well with the required 3D chemical mapping needed to picture the complex systems and interfaces of SFMN materials. The HR S/TEM imaging capability of Talos will fit also the required resolution for mapping the morphology and crystalline structure of our perovskites. Data will be analyzed and managed by Dr. Marcello Marelli, using commercial software, already in use at CNR-SCITEC labs (ImageJ, GMS, Origin and others).

3. Summary of previous experimental proposals or characterisation

Screening analysis on SFMN-exsolved systems was carried out at CNR-SCITEC ISTeM Labs (laboratorio di microscopia Elettronica) in Milano with a ZEISS LIBRA200 Electron microscopy.
Analysis highlights the formation of segregated nanoparticles (10 to 40 nm size in range) exsolved from the bulk crystalline perovskite. These nanoparticles are enriched in Ni. The Proposal PI, Dr. Marelli, is a senior user at ISTeM Labs and recorded the TEM analysis.





Representative STEM (on the left side) and TEM (on the right side) micrographs of SFMN-exsolved systems

4. Justification of experimental proposals request

I request access to the HRTEM Talos instrument since offers a state of art analysis both for high-resolution imaging and EDS qualitative/quantitative elemental maps. These analyses will integrate the low-mag screening test images and help to fully characterize these promising materials, establishing a strong connection between structure and activity. I Request 3 days of machine time counting 1 sample/day in the first two days (HR S/TEM imaging, EDS general analysis, and elemental mapping) and one/two samples on the third day (experience on previous samples could speed up the analysis time). No sample preparation time will be requested.