Experimental report

12/09/2023

Proposal: 5-25-283 **Council:** 10/2022

Title: The fluorination reaction of La2NiO4 studied by in situ neutron powder diffraction

Research area: Chemistry

This proposal is a new proposal

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Samples: La2NiO4 PVDF mixture 1:1.5
La2NiO4 PVDF mixture 1:1
La2NiO4 PTFE mixture

Instrument	Requested days	Allocated days	From	To
D20	3	3	19/05/2023	22/05/2023

Abstract:

The synthesis of new oxyfluorides with Ruddlesden-Popper structure is a current topic in solid state chemistry because of their wide range of different physical properties as well as their possible application as electrode materials in F-ion batteries. Understanding the formation chemistry of oxyfluorides is crucial for accessing new metastable products and for optimizing reaction conditions. By in situ XRD experiments insights into the reaction pathway of the fluorination reaction of La2NiO4 were achieved. The reaction was found to progress through three metastable reaction intermediates with different structures solved from X-ray and neutron powder diffraction. Within this proposal, we will observe the fluorination reaction of La2NiO4 in situ and we plan to obtain reliable reaction time-dependent coordinates and occupation factors for the anionic sub lattice of the reaction intermediates by Rietveld refinements. By this, we aim to derive a reaction mechanism, which we propose to consist of several insertion/substitution steps. In-depth knowledge of the reaction mechanism will enable the targeted synthesis of new, even less stable oxyfluorides in the future.

The fluoriation reaction of La_2NiO_4 studied by *in situ* neutron powder diffraction (experiment 5-25-283)

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Objectives: The reaction of oxides with the fluoro polymers polyvinylidene fluoride (PVDF) and poly tetrafluoroethylene (PTFE) has been proven to be an excellent way for preparing new oxyfluorides in recent years. In our previous *in situ* XRD experiments we found that the reaction of La_2NiO_4 consists of several partially fluorinated reaction intermediates[1]. The aim of the proposed experiment was to perform *in situ* neutron powder diffraction experiments on the fluorination reaction of La_2NiO_4 targeting two different oxyfluorides $La_2NiO_3F_2$[2] and $La_2NiO_{2.5}F_3$[1] as well as more then 4 different reaction intermediates. We plan to obtain precise atom coordinates and occupation numbers for the anionic sublattice By Rietveld refinements of the reaction intermediates enabling a better understanding of the reaction pathway of such fluorination reactions.

Experimental Details: All experiments were performed at D20 in high-resolution mode at $\lambda = 1.87$ Å. The samples were contained in custom low background sapphire single-crystal cells within a modified version of the *in situ* setup developed by Kohlmann et al.[3] which is shown in Fig.1. Heating was realized by using two commercially available heat guns which were positioned in nozzle to sample distance of 60 mm in an angle of 120° to each other. The sample temperature was monitored by a pyrometer. This setup was chosen instead of the proposed laser heating as the reaction intermediates all showed different absorption behavior to the IR-Laser throughout the fluorination reaction demanding for a constant readjustment of the laser power. Additionally, safety measures were highly reduced and the setup was simplified by this approach. Rietveld refinements were performed with GSAS II, and the instrument parameters were refined based on a preliminary Si reference scan.

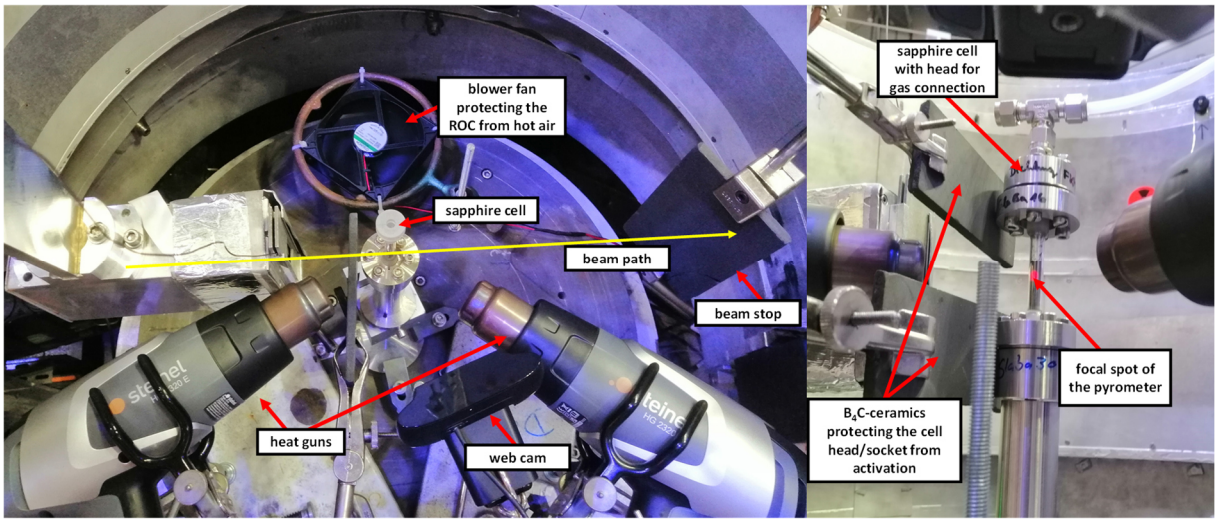

Fig. 1: experimental setup consisting of the sapphire cell, two heat guns, a web cam, a pyrometer (not in the picture, and an upwards pointing blower fan directing the hot air away from the radial oscillating collimator (ROC).

Results and Discussion: In a first test the temperature displayed by the pyrometer was verified by the thermal unit cell evolution of NaCl. Diffraction patterns were recorded for 5 min in steps of 50°C up to 650°C (heat gun temp.) after 5 min equilibration time. Hereby similar temperature values (pyrometer/unit cell evolution) were obtained und the pyrometer was therefore used for temperature monitoring in the 4 subsequent experiments.

Experiment#1 La_2NiO_4:PVDF (ratio 1:1) (NUMOR 225638 to 225809): The sapphire cell was equipped with its usual gas adapter head (shown in fig. 1) and air was passed over the reaction mixture by a membrane pump. The use of a dynamic air atmosphere was the result of several preliminary XRD experiments where a dynamic atmosphere was proven to speed up the reaction. The diffraction patterns of this experiment are shown as contour plot in Fig.2 (left). In contrast to the preliminary XRD results a very slowly progressing reaction was found yielding only signals of a first reaction intermediate with orthorhombic structure after 9 h at T_{max} (in comparison, this is usually observed after 1 to 2 h in XRD experiments). To speed up the reaction, the temperature was raised twice from 366 °C to 372 °C (n225754) and 378 °C (n225784). This resulted in no significant increase in reaction speed and the experiment was stopped after 14 h in order to keep up with the foreseen schedule.

Experiment#2 La_2NiO_4:PVDF (ratio 1:1.5) (NUMOR 225814 to 225907): The setup was kept the same as in #1 but data acquisition time was increased to 10 min aiming for an improved signal to noise ratio in order to compensate for the increased background due to incoherent scattering of hydrogen. The reaction also progressed unexpectedly slow (This reaction was previously found to progress even faster than the 1:1 reaction) which is why the cell head was removed in n225823. After removal of the cell head the reaction started immediately which can be seen in the shift of reflections in the contour plot of Fig.2 (right). The reason of the slow reaction was therefore found in a reduced atmospheric pressure due to the venturi effect caused by the Swagelok T-piece connector. This demonstrates that air (oxygen) is needed for this reaction The experiment was stopped after 15 h. The final diffraction patterns still contained weak reflections of the starting oxide as well as reaction intermediates which is due to a misalignment of the heated zone and the neutron beam. Here the position of the heated zone should be controlled by thermal imaging in future experiments.

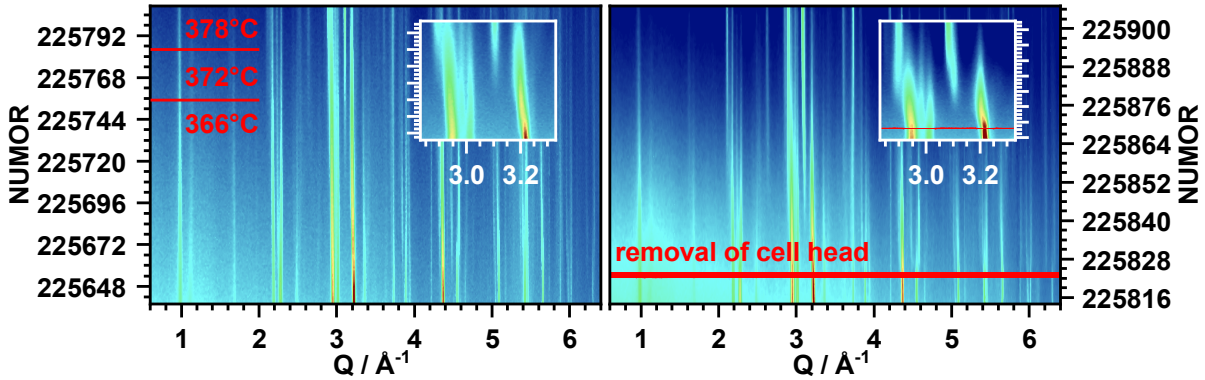

Fig. 2: Contour-plot of the diffraction patterns obtained for the reaction of La_2NiO_4/PVDF mixtures in the ratio of 1:1; experiment#1: (left), and the ratio of 1:1.5; experiment#2 (right).

Experiment#3 La_2NiO_4:PVDF (ratio 1:1) (NUMOR 225909 to 225970): This experiment was additionally performed as repetition of experiment#1. The sapphire cell was directly used as open crucible without the gas adapter head to ensure correct ventilation. By this experiment we successfully captured the whole reaction in the course of 10 h and the contour-plot of the diffraction patterns is shown in Fig. 3 (left).

Experiment#4 1 La_2NiO_4:PTFE (ratio 1:1) (NUMOR 225972 to 226033): In this final experiment PTFE was used as the fluorine source with the aim of comparing the reactivity and fluorination mechanism of both fluorine sources. The use of PTFE which does not contain hydrogen additionally suppresses the incoherent scattering background of experiements#1-3, enabling a more precise identification of weaker reflections. The contour-plot of this experiment is shown in Fig. 4 (right). Unfortunately, the reaction was stopped after 11 h due

to the end of the allocated beamtime, leaving this reaction unfinished. The rather slow reaction rate of PTFE was also found in preliminary XRD studies which is one downside to the use of PTFE as fluorination regent.

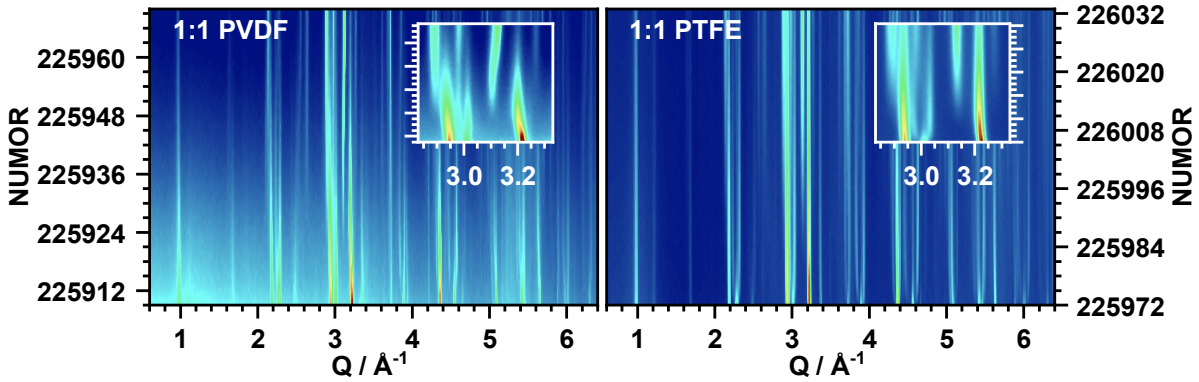

Fig. 3: Contour-plot of the diffraction patterns obtained for the reaction of a La_2NiO_4/PVDF mixture in the ratio of 1:1; experiment#3 (left), and a La_2NiO_4/PTFE mixture in the same 1:1 ratio; experiment#4; (right). Diffraction patterns were obtained with 10min acquisition time for both experiments.

Conclusion and first Refinements: The complete fluorination reaction of La_2NiO_4 with PVDF as fluorine source of was successfully captured by *in situ* neutron diffraction in a self-made setup for both targeted compounds ($La_2NiO_3F_2$ and $La_2NiO_{2.5}F_3$). First Rietveld refinements were performed (an exemplary Rietveld Plot is shown in Fig. 4) for all experiments and the following information are obtained by now:

1. Reflections of two orthorhombic reaction intermediates were identified in both fluorination reactions: **1^{1st}** *Bmab*; **2nd**: orthorhombic ***P*-centered** (due to reflections (338), (009), (031) and (310) corresponding to the *Fmmm* unit cell), **this intermediate was not identified in the preliminary *in situ* XRD studies**.
2. The **3rd** reaction intermediate possesses a monoclinic structure with SG *C*2/*c* which was previously solved for the 1:1.5 reaction based on TOF-NPD data of a quenched sample. By the here obtained data we conclude that this intermediate is not the same for both reactions.
3. The reaction with PTFE progresses through similar intermediates with different occupation of the anionic positions, here a slightly different reaction mechanism seems likely.

Precise determination of the correct space group of the second intermediate as well as the extraction of reliable anionic positions and occupation numbers will be targeted in the ongoing refinements the *failed* experiment#1 will be very useful for this purpose as the reflections of the 1st and 2nd intermediate are verry well resolved due to the slow reaction. The data evaluation will be supported by MAS 19F-NMR experiments which are currently performed in cooperation with Prof. Jörn Schmedt auf der Günne (Uni Siegen) for quenched reaction mixtures.

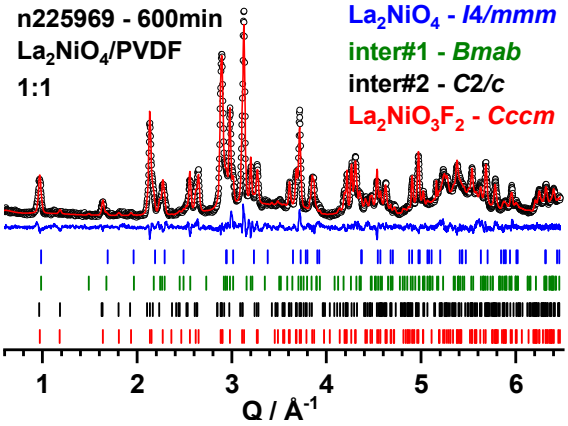

Fig. 4: RV-Plot of the refinement of n 225969 taken from the reaction of La_2NiO_4 and PVDF in a 1:1 ratio (experiment#3).

[1] J. Jacobs et al. *Inorg. Chem.* **2021**, *60*, 13646–13657. [2] K. Wissel et al., *Inorg. Chem.* **2018**, *57*, 6549–6560. [3] R. Finger et al., *J. Appl. Crystallogr.* **2021**, *54*, 839–846.