# Monitor the oxidation state and fine structures of mixed anion cathode materials during charge/discharge process in-operando conditions

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### 1. 背景と研究目的

Materials for Lithium and Sodium batteries are an active field of research. Anionic substitution is a path to improve battery performance. In this proposal, we measured materials with and without different anionic substitutions to search for changes in the cation environment. The materials to be tested are FMN (NaFe<sub>0.4</sub>Mn<sub>0.3</sub>Ni<sub>0.3</sub>O<sub>2</sub>, NaFe<sub>0.4</sub>Ni<sub>0.3</sub>Mn<sub>0.3</sub>O<sub>2-x</sub>S<sub>x</sub>,) and NCM (LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>, and LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2-x</sub>F<sub>x</sub>). Also, the design of a cell for in-operando conditions was tested using NaFe<sub>0.4</sub>Mn<sub>0.3</sub>Ni<sub>0.3</sub>O<sub>2</sub> as a cathode.

#### 2. 実験内容

Due to the air sensitivity of cathode materials (NCM and FMN), the samples were prepared in a glove box. Oxides were mixed with BN in proportions according to the cationic composition to get a jump equal to 1. The mixture of oxides and BN were pressed to 10kN in a 10mm die. The pellets were packed into aluminized bags with Kapton windows and sealed into an argon atmosphere to avoid air exposure. For In-operando measurements of FMN bare oxide, a 5 mm hole was performed in the coin cells and covered with Kapton tape to allow the normal operation of the cell. Correct operation of the cells was performed in the lab prior to the synchrotron shift. All samples were measured in Q-XAS, with measurements time of 2 minutes. The K-edges of each metal (Mn, Fe, Co, and Ni) were measured.

#### 3. 結果および考察

For the system NCM, XAFS spectra showed not relevant changes between the bare oxide and the oxyfluoride. In the case of the FMN, the comparison of the bare oxide and oxisulfide, the Ni edge exhibit visible changes (See figure), while the Fe was less stronly modified and Mn shows not differences. These observations indicates that the sulphur is located with the following preference: Ni > Fe > Mn.

In the case of in-operando measurement, the modified coin cell allowed to make measurements with good signal-to-noise in the Mn K-edge. Also, the battery was operative and the voltage was raised from 2.8 V to 4.2 V using a potentiostat, taking QXAS spectra at 2.8V and every 100mV from 3.8 to 4.2V. The successful results of the in-operando cell allow us to perform in-operando measurements in the future.



## 4. 参考文献

1. Kimijima et al., Cryst. Growth Des. 2016, 16, 5, 2618–2623