BIO Web of Conferences **129**, 08009 (2024) https://doi.org/10.1051/bioconf/202412908009
EMC 2024

MicroReactor for battery materials synthesis in SEM

Libor Novak[1], Mr. Vojtěch Kundrát[2], Mr. Petr Hlavenka[1]
[1]Thermo Fisher Scientific, Brno, Czechia, [2]Weizmann Institute of Science, Rehovot, Israel

Background incl. aims
In-situ SEM can help with understanding and optimization of processes forming (nano-)materials usable in electronic devices and energy storage systems. The high-temperature synthesis of these materials often happens in reactive, explosive, or harmful environments.
This study aimed to prove the functionality of the MicroReactor device for in situ SEM imaging during experiments requiring reactive gases (such as pure hydrogen or hydrogen sulfide) that result in the synthesis of the currently used and possible future battery materials.

Methods
MicroReactor device [1] equipped with a MEMS heating & biasing chip [2] was used in Helios G4 UX and Scios DualBeam systems. The MicroReactor's low-volume reaction chamber, coupled with a retractable lid enabling work with reactive gases during SEM operation and open access for sample preparation by FIB, assures improved process cleanliness and safety compared to an environmental SEM. In-lens detectors of the SEM column as well as STEM or 4D STEM detectors placed below the transparent MEMS chip can monitor changes in the processed sample. Real-time gas analysis of reaction products is possible on the outlet line connected to the reaction volume. After gas-assisted processing, EDS and EBSD analyses can follow while the sample remains heated up to 1200°C. In the latest design, the MicroReactor sample holder can be transferred in argon between a glove box and a FIB-SEM chamber.

Results
Three novel applications of MicroReactor will be presented.
1) The capacity and lifetime of NMC cathode in Li-ion battery depend on the parameters of the high-temperature lithiation process. The MicroReactor can be used to follow morphological changes of the NMC particles which indicate the state of lithiation. An example of a possible way of lithiation process, that uses LiOH as the source material, is shown in the graphics. A pure oxygen environment was selected in the MicroReactor to remove the hydrogen from the final cathode material.
2) The growth of tungsten suboxide W18O49 nanowhiskers from WO3-SiO2 nanofibers was studied in the MicroReactor [1]. Reduction of the WO3 in nanofibers was possible at 800°C in a hydrogen environment (100 Pa). The tunability of redox properties, thermal stability, and large surface area make

tungsten suboxides promising materials for applications in energy storage systems.

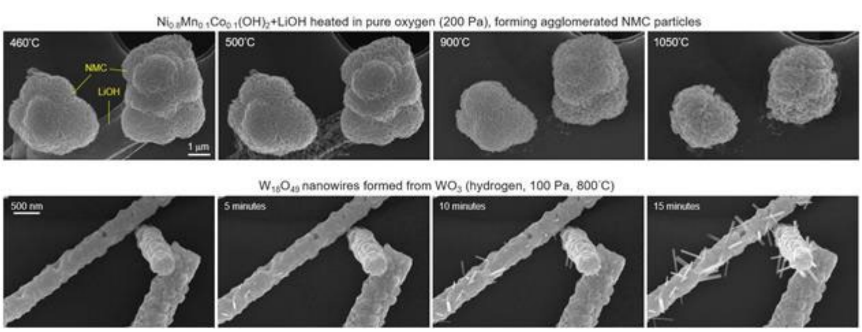
3) Tungsten disulfide is a 2D material with unique properties applicable in many fields including electronics, catalysis, and energy storage. A modified pumping system of the Scios DualBeam equipped with MicroReactor enabled the injection of hydrogen sulfide & hydrogen mixture which was essential for the successful sulfidation of a sample containing W18O49 nanowires. Using a combined in-situ SEM and ex-situ TEM analysis, it was possible to explain the mechanism of WS2 synthesis from tungsten suboxides for the very first time [3].

Conclusion

The three presented examples demonstrate novel applications of the MicroReactor in SEM. The second example proved process cleanliness sufficient for sample reduction at high temperatures. The creation of this abstract proves the possibility of safe work with dangerous gases in the third example, which at the same time demonstrates the possibility of exploring the fundamental behavior of chemical processes.

In addition to the conclusions summarized in [1] and [3], it can be stated that in situ SEM equipped with the MicroReactor is a useful complement to the more widespread TEM in-situ techniques, which can bring new insight with several benefits. SEM excels in capturing reaction kinetics at a larger scale and provides topographical information in the surface-sensitive signal of secondary electrons. The presented technique can further be combined with ex-situ TEM analysis or with ETEM, both on the same MEMS chip that is used in SEM.

Graphic:



Keywords:

In-situ SEM, MicroReactor, batteries, WS2

Reference:

[1] Kundrat, V. et al. Cryst. Growth Des. 2024, 24, 1, 378–390, doi: 10.1021/acs.cgd.3c01094
[2] Mele, L. et al. Microscopy Research and Technique 2016, 79, 239. https://doi.org/10.1002/jemt.22623
[3] Kundrat, V. et al. ACS Nano 2024, 18, 19, 12284-12294. https://pubs.acs.org/doi/10.1021/acsnano.4c01150