MAX phase-based nanocomposites for LIBs negative electrodes investigated by multi-approach TEM analysis

Irene Ostroman[1], Dr. Cameron Duncan[1], Mrs. Beatrice Ferrari[1], Mrs. Maria Giulia Bravi[1], Dr. Antonio Gentile[2], Dr. Stefano Marchionna[2], Dr. Chiara Ferrara[1], Dr. Taewon Kim[3], Dr. Changhyun Park[3], Dr. Chanhee Lee[3], Prof. Hyun-Wook Lee[3], Prof. Riccardo Ruffo[1], Prof. Giovanni Maria Vanacore[1]
[1]Università degli Studi di Milano-Bicocca - UNIMIB, Milano, Italy, [2]Ricerca sul Sistema Energetico - RSE S.p.A, Milano, Italy, [3]Ulsan National Institute of Science and Technology - UNIST, Ulsan, Republic of Korea

Background incl. aims
In a landscape where the global demand for clean and reliable energy sources, and the need to mitigate the environmental impacts of fossil fuels, are constantly growing, lithium-ion batteries (LIBs) represent the most widespread energy storage technology, due to their reliability and excellent electrochemical performance. Nonetheless, the drawbacks of graphite, the most used negative electrode in LIBs, pose the need to study materials that present better outputs. In the limited landscape of alternative anodic materials, one of the most interesting is the family of MXenes: 2D materials with Mn+1XnTx stoichiometry (M represents a transition metal, X carbon or nitrogen, T the functionalization of the layers). However, these materials are obtained by etching the corresponding MAX phase precursor with HF, a seriously hazardous operation. To overcome the issue, we changed the paradigm and thermally treated Sn-doped MAX phases with different levels of Sn doping, obtaining peculiar MAX nanocomposites, and employing them as anodic materials in LIBs. [1] Since the key to understanding their electrochemical behavior lies in the morphology, crystal structure, and formation mechanism of the nanostructures, a multi-approach Transmission Electron Microscopy (TEM) analysis has been the main character in the investigation of the materials, consisting of static High-Resolution TEM (HRTEM), Operando TEM upon electrochemical materials lithiation [2] and pump-probe dynamic Ultrafast TEM (UTEM). [3]

Methods
The Ti3Al(1-x)SnxC2 MAX phase samples with nominal x = 0, 0.4, and 0.7 were synthesized through Spark Plasma Sintering (SPS). They were heated in air at 600°C and studied as anodic materials in LIBs by galvanostatic cycling with potential limitation (GCPL) in two-electrode coin cells. The sample were characterized by neutron and X-ray diffraction, CHNS, thermal gravimetric analysis, Scanning Electron Microscopy and Raman spectroscopy. Static HRTEM was executed with a JEOL JEM 2100 Plus operated at 200 kV at UNIMIB; Operando electrochemical TEM measurements were obtained with a JEOL JEM 2100 Plus at 200 kV at UNIST coupled to a Nanofactory Instruments in-situ Dual-Probe sample-holder used to apply bias and execute the lithiation. The pump-probe UTEM measurements are going to be acquired with a JEOL JEM 2100 coupled with a fs PHAROS laser in stroboscopic mode: the 1030 nm IR laser is both used as the pump and upconverted into UV light used to generate the photoelectron pulses used as the probe.

Results
The electrochemical performances show a very large improvement for the oxidized samples; moreover, the cells show a remarkably increasing capacity for a higher Sn content: it reaches 200 mAh g-1 for Sn0.4_Ox and 250 mAh g-1 for Sn0.7_Ox at 1 C, more than double to the non-Sn-doped material. Moreover, the samples showed an excellent value of Coulombic Efficiency (99.6%) and good stability upon cycling. The structural analysis evidenced the appearance of rutile and SnyTi(1-y)O2 mixed oxides in the thermally treated samples, and the HRTEM imaging highlighted the morphology of such nanometric crystallites on the MAX

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phase surface as shown in Figure 1. Since the MAX phase is inert, the potential profiles from the GCPL suggest that for the LIBs the measured capacity is due to mixed mechanisms of intercalation, conversion, and alloying in the nanostructured oxide composite. The main contribution of SnO2 conversion and alloying has been confirmed thanks to the operando electrochemical TEM analysis, which shows the enlargement of the surface structures (clearly depicted in Figure 2), typical of the mentioned mechanisms.

According to our analysis, the presence of Sn lowers the MAX phase resistance to oxidation, giving a lower oxidation temperature and a higher percentage of oxides, which is confirmed also by CHNS; for a complete understanding of the process, as sketched in Figure 3, pump-probe dynamic UTEM measurements will be crucial to unveil the onset of the transient structural modification upon laser heating which leads to oxidation in the presence of oxygen.

Conclusions

Our study has highlighted that the unaltered conductive MAX phase cores show a beneficial role to the surrounding oxide nanoparticles since they can ensure sufficient electrical contact. In addition, as testified by the good stability of the samples, the SnyTi(1-y)O2 solid solution prevents the huge volume changes that pure SnO2 particles typically show, which cause an important loss of capacity after a few cycles due to active material shattering. Our investigation underscores the indispensable role of a diverse TEM analysis in elucidating the electrochemical behavior and structural transformations of the Ti/Sn oxides and Sn-doped MAX phase composite, paving the way for the rational design and optimization of such nanocomposites for next-generation LIBs.

Graphic:

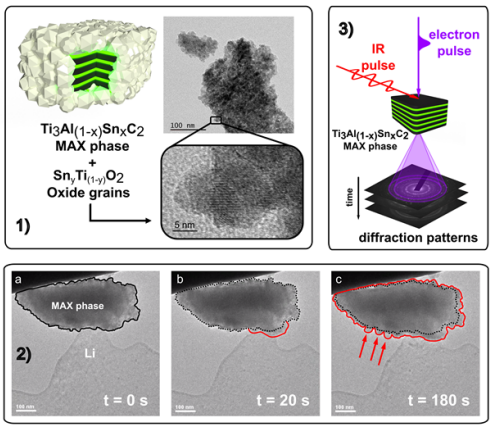

Figure 1. Sketch of an oxidized MAX phase grain and HRTEM images of the sample Sn0.7_Ox.
Figure 2. A sequence of images taken with operando TEM of a Sn0.7_Ox grain upon lithiation. a) No contact and no biasing; b) 20 s after starting bias, the oxide nanoparticles close to the contact spot show enlargement; c) 180 s after starting bias, all the nanoparticles are enlarged, three evident round nanoparticles marked with arrows.
Figure 3. Scheme of the pump-probe dynamic UTEM measurements. Transient structural modification (which leads to oxidation in the presence of oxygen) of a MAX phase grain is stimulated by laser heating.

Keywords:

Energy-Storage, lithium-metal-batteries, Ultrafast-TEM, pump-probe, operando-TEM

Reference:

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