

The Impact of Transition Metal Dopants in Conversion/Alloying Lithium-Ion Anodes on Structure, SEI Formation and Electrochemical Performance

Tobias Eisenmann,^{1,2} Adele Birrozzi,^{1,2} Angelo Mullaliu,^{1,2} Jakob Asenbauer,^{1,2} Gabriele Giuli,³
Angela Trapananti,⁴ S. Javad Rezvani,^{5,6} Stefano Passerini,^{1,2} Dominic Bresser,^{1,2}

¹Helmholtz Institute Ulm (HIU), Helmholtzstrasse 11, 89081, Ulm, Germany

²Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany

³School of Science and Technology, Geology Division, University of Camerino, 62032 Camerino, Italy

⁴School of Science and Technology, Physics Division, University of Camerino, 62032 Camerino, Italy

⁵INFN, Laboratori Nazionali di Frascati, Via Enrico Fermi 54, Frascati 00044, Italy

⁶Consiglio Nazionale delle Ricerche (CNR) IOM-CNR, Laboratorio TASC Basovizza SS-14, km 163.5,
Trieste 34149, Italy

Tobias.eisenmann@kit.edu

Lithium-ion batteries (LIBs) power most of today's portable electronics, electric vehicles (EVs) and many other devices.^[1] In order to prevail in this superior position, however, LIBs will have to be continuously improved. The state-of-the-art material for the anode side is graphite, which exhibits a relatively high specific capacity and a low de-/lithiation potential.^[2] However, customer expectations in, for instance, the EV market are high, and the low volumetric capacity and the incapability for fast charging of graphite anodes call for alternative anode active materials.

Alloying and conversion materials typically offer both higher capacities and better rate capability than graphite and are, therefore, suitable candidates for next-generation LIBs.^[3,4] However, both classes also suffer from distinct intrinsic challenges: Alloying materials undergo substantial volume variations upon electrochemical de-/lithiation, which eventually results in material exfoliation, whereas the wide de-/lithiation potentials and large voltage hysteresis of conversion materials limits the overall energy density and efficiency. The combination of both mechanisms in one active material – so-called conversion/alloying materials (CAMs) – allows for the mitigation of the aforementioned drawbacks by synergistically exploiting the advantages of each individual class.^[5] When partially replacing the alloying metal in zinc or tin oxide with a transition metal (TM), for instance, the resulting active materials exhibit higher reversible capacities and lower de-/lithiation potentials when compared to their non-doped counterparts. Nevertheless, the precise role of these TM dopants and how they affect the de-/lithiation mechanism on the local atomic scale and the solid electrolyte interphase (SEI) formation remains unresolved.

Herein, we tackle these uncertainties by a comprehensive and exemplary analysis of TM-doped zinc oxide and germanium oxide *via* – among other techniques – X-ray absorption spectroscopy (XAS). The combination of XAS in the soft and hard X-ray regime, i.e., complementary surface and bulk sensitive modes, allowed us to (i) gather insights into the impact of the transition metal doping, in terms of both concentration and chemical nature, concerning the de-/lithiation mechanism at the local atomic scale,^[6–8] (ii) elucidate the effect of the TM location in the structure and the application of a carbon coating on the electrochemical performance,^[9] and (iii) unravel the influence of different TMs on the SEI formation.^[10] These results do not only shed light on the herein investigated materials, but bear insights on commonly overlooked parameters that are affecting the performance of metal oxides in general; thus, rendering them of great significance for the development of alternative anode materials for LIBs in the future.

References

- [1] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B. Lestriez, P. Novák, M. Petráňková, W. Porcher, S. Trabesinger, M. Wohlfahrt-Mehrens, H. Zhang, *J. Power Sources* **2020**, 479, 228708.
- [2] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, *Sustain. Energy Fuels* **2020**, 4, 5387.
- [3] M. N. Obrovac, V. L. Chevrier, *Chem. Rev.* **2014**, 114, 11444–11502.
- [4] M. D. Bhatt, J. Y. Lee, *Int. J. Hydrogen Energy* **2019**, 44, 10852–10905.
- [5] D. Bresser, S. Passerini, B. Scrosati, *Energy Environ. Sci.* **2016**, 9, 3348–3367.
- [6] G. Giuli, T. Eisenmann, D. Bresser, A. Trapananti, J. Asenbauer, F. Mueller, S. Passerini, *Materials* **2017**, 11, 49.
- [7] A. Trapananti, T. Eisenmann, G. Giuli, F. Müller, A. Moretti, S. Passerini, D. Bresser, *Mater. Today Chem.* **2021**, 20, 100478.
- [8] T. Eisenmann, A. Birrozzi, A. Mullaliu, J. Asenbauer, G. Giuli, A. Trapananti, L. Olivi, D. Geiger, U. Kaiser, S. Passerini, D. Bresser, *J. Phys. Chem. C* **2021**, 125, 8947–8958.
- [9] T. Eisenmann, A. Birrozzi, A. Mullaliu, G. Giuli, A. Trapananti, S. Passerini, D. Bresser, *J. Electrochem. Soc.* **2021**, 168, 030503.
- [10] T. Eisenmann, J. Asenbauer, S. J. Rezvani, T. Diemant, R. J. Behm, D. Geiger, U. Kaiser, S. Passerini, D. Bresser, *Small Methods* **2021**, 5, 2001021.