

Supporting Information

Determination of the volume changes occurring for conversion/alloying-type

Li-ion anodes upon de-/lithiation

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Experimental Section

Material synthesis and characterization

Carbon-coated ZnFe_2O_4 ($\text{ZnFe}_2\text{O}_4\text{-C}$) was prepared according to Bresser et al.,¹ i.e., by mixing 1.0 g of ZnFe_2O_4 nanoparticles (<100 nm, Sigma-Aldrich) with 0.5 g of sucrose in 2.0 g of water. The mixture was homogenized by planetary ball milling and dried at 80 °C. Finally, the dried powder was thermally treated at 500 °C for 4 h under argon atmosphere to obtain the carbonaceous coating. $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O-C}$ was synthesized as reported by Bresser et al.² In brief, an aqueous solution of zinc(II) gluconate hydrate (ABCR) and iron(II) gluconate dihydrate (Aldrich) was prepared, based on the targeted stoichiometric ratio. The water was evaporated at 160 °C and the remaining solid phase was calcined for 3 h at 450 °C under air. The carbon coating was performed in the same way as for $\text{ZnFe}_2\text{O}_4\text{-C}$. $\text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2\text{-C}$ was synthesized according to Ma et al.³ In brief, an aqueous solution of tin(II) acetate (Aldrich) and acetic acid (Aldrich) was gradually added to an aqueous solution of iron(II) gluconate dihydrate (Aldrich) and sucrose (ACROS). The water was evaporated at 160 °C and the resulting solid material was calcined for 3 h at 450 °C under air. The carbon coating was performed in the same way as for the other two compounds. The comprehensive physicochemical characterization is reported in the aforementioned references. The density of the materials was determined using a Micro-UltraPyc 1200e pycnometer from Quantachrome and helium as analysis gas. The carbon content was determined *via* thermogravimetric analysis (TGA) using a Q5000 from TA Instruments.

Electrode preparation

All electrodes were prepared following the same procedure. To start with, the active material and carbon black (Super C65, Imerys) were added to a 1.25 wt% solution of sodium carboxymethyl cellulose (CMC, Dow Wolff Cellulosics) in deionized water and mixed by planetary ball-milling (Pulverisette 4, Fritsch) for 2 h. The solid content composition was 75 wt% active material, 20 wt% carbon black, and 5 wt% CMC. The homogenized slurry was cast on dendritic copper foil (Schlenk) using a laboratory-scale doctor blade. The wet film thickness was set to 120 μm . The resulting electrode sheets were dried at 80 °C for 5 min and overnight at room temperature. Subsequently, disc electrodes ($\varnothing = 10$ or 12 mm)

were punched and dried under vacuum at 120 °C for 12 h. The average active materials mass loading was about 1.5 mg cm⁻².

Operando dilatometry

Operando electrochemical dilatometry was performed using an ECD-3 Nano Dilatometer cell (EL-CELL) with a rigid, porous ceramic T-frit, serving as separator and soaked with a 1M solution of LiPF₆ in 3:7 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The diameter of the working electrodes was 10 mm. The precise mass loading and the initial electrode thickness were determined prior to the cell assembly. Lithium metal (Honjo, battery grade) was used as counter and reference electrode. During the measurement, the temperature was kept at 20 °C by means of a climatic chamber (Binder KB 23). Galvanostatic cycling was carried out using a SP-150 potentiostat (BioLogic), applying a specific current of 50 mA g⁻¹ for the first cycle and 100 mA g⁻¹ for the following cycles.

Ex situ cross-sectional SEM analysis

For the *ex situ* cross-sectional SEM analysis, the electrodes were stuck on customized copper current collectors using conductive copper tape. The electrode cross section was analyzed *via* scanning electron microscopy (SEM; Zeiss Crossbeam 340 field-emission electron microscope), employing focused ion beam (FIB; Capella; Ga source) milling and energy-dispersive X-ray spectroscopy (EDX; Oxford Instruments X-MaxN). After having studied the cross section of the pristine electrodes, they were fully lithiated (cut-off: 0.01 V vs. Li⁺/Li) in Swagelok-type T-cells with lithium metal serving as counter and reference electrodes. The electrolyte was the same as in the case of the dilatometry experiments. Subsequently, the cells were disassembled in the glove box under argon atmosphere and transferred to the SEM again using an airtight transport box. This procedure was repeated for the subsequently delithiated electrodes (cut-off: 3.0 V vs. Li⁺/Li). Note that the cross section required some additional polishing *via* FIB milling (ca. 1 μm) after the lithiation and delithiation due to the presence of electrolyte decomposition products.

Table S1. Summary of experimentally determined bulk densities of the pristine and carbon-coated CAMs as well as the literature values for the different compounds formed upon lithiation.

Compound	Density / g cm ⁻³
ZnFe ₂ O ₄	5.6
Zn _{0.9} Fe _{0.1} O	5.6
Sn _{0.9} Fe _{0.1} O ₂	6.9
ZnFe ₂ O ₄ -C	4.3
Zn _{0.9} Fe _{0.1} O-C	4.7
Sn _{0.9} Fe _{0.1} O ₂ -C	4.7
Li ₂ O	2.0 ⁴
Fe	7.9 ⁵
Zn	7.1 ⁶
Sn	7.29 ⁷
LiZn	4.08 ⁸
Li _{4.4} Sn	2.57 ⁷

Table S2. Summary of the volumetric capacities of ZnFe_2O_4 , $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$, and $\text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2$ for the complete conversion/alloying reaction, the conversion reaction only, and the alloying reaction only, considering (a) the bulk density of the pristine material as experimentally determined, and the estimated densities after (b) the complete conversion/alloying reaction and (c) after the conversion reaction only.

Active Material	Volumetric capacity (total) / mAh g ⁻¹	Volumetric capacity (conversion) / mAh g ⁻¹	Volumetric capacity (alloying) / mAh g ⁻¹
ZnFe_2O_4	5603 ^(a) /3314 ^(b)	4980 ^(a) /3174 ^(c)	623 ^(a) /368 ^(b)
$\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$	5410 ^(a) /3074 ^(b)	3731 ^(a) /2626 ^(c)	1679 ^(a) /954 ^(b)
$\text{Sn}_{0.9}\text{Fe}_{0.1}\text{O}_2$	8272 ^(a) /3534 ^(b)	4157 ^(a) /2825 ^(c)	4115 ^(a) /1758 ^(b)

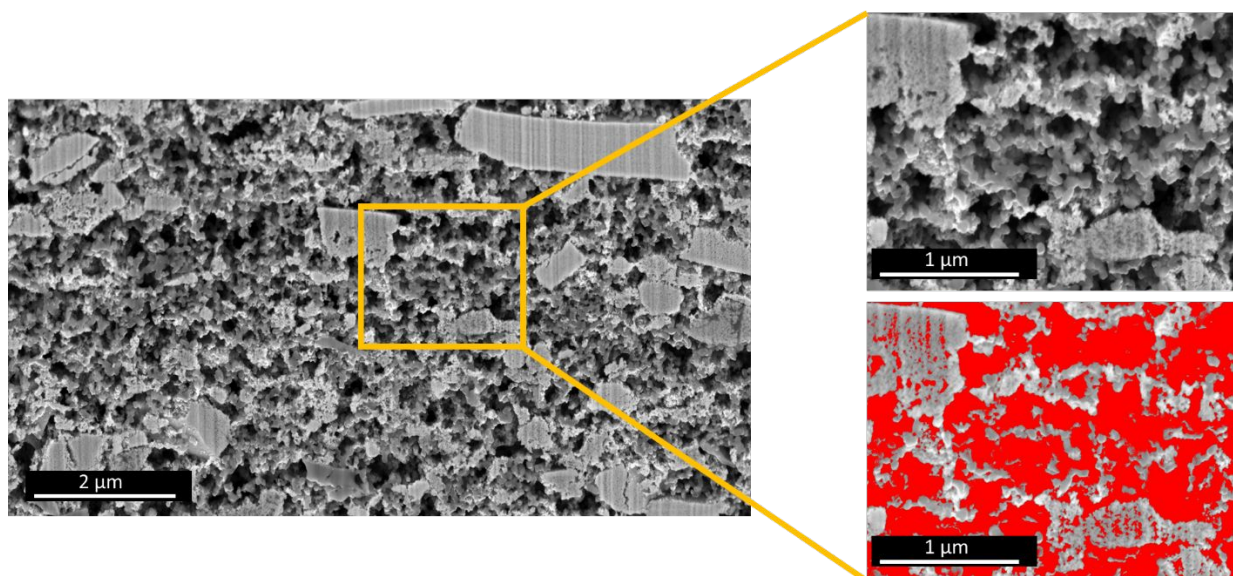


Figure S1. SEM micrograph of the cross section of a pristine $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O-C}$ electrode (left; see also **Figure 3c**) with a magnification of the highlighted area and determination of the porosity (in red) *via* computational segmentation (right).

References

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