Proof of concept: Ti-doped zinc ferrite for application as cathode material in zinc ion batteries

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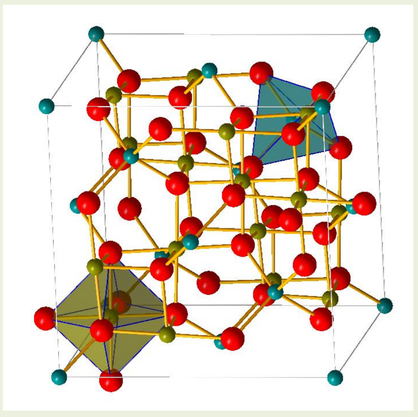
Patent pending

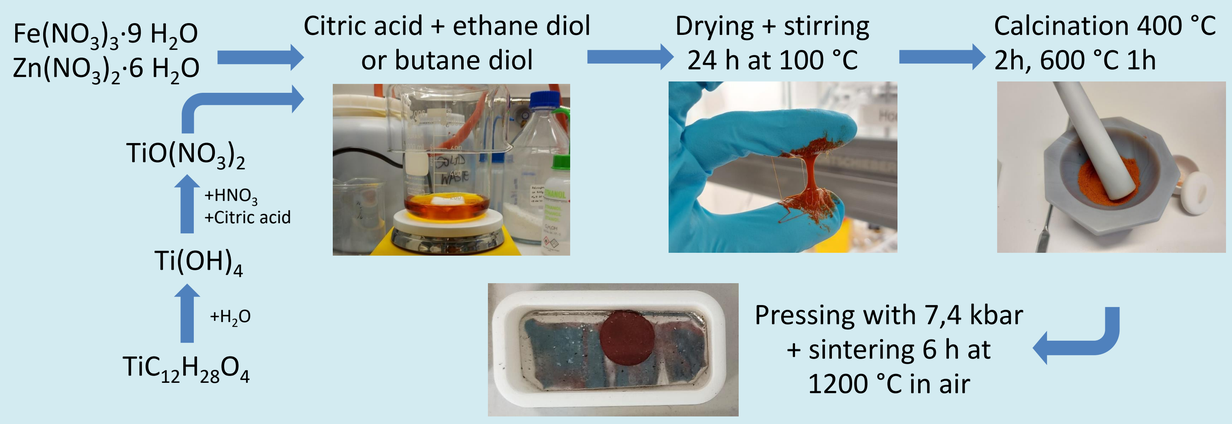
Material



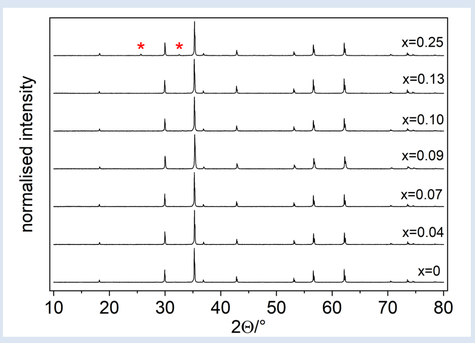
$ZnFe_2O_4$ is a well-known spinel material which is applied in a variety of areas ranging from anode material in lithium-ion batteries to photo-electrochemical water splitting and high-density magnetic data storage [1]. By doping with a tetravalent cation on the B position (Ti^{4+}), zinc vacancies should develop which could be beneficial for the application of $ZnFe_2O_4$ as cathode material in zinc ion batteries [2,3].

$$2TiO_2 \xrightarrow{ZnFe_2O_4} 2Ti_{Fe}^{\circ} + V_{Zn}'' + 4O_O^x$$

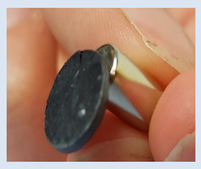
Synthesis $ZnFe_{2-x}Ti_xO_4$



(Micro-) Structural analysis $ZnFe_{2-x}Ti_xO_4$ pellets

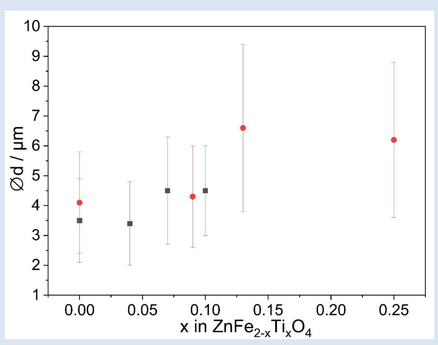


All samples can be picked up with a magnet.



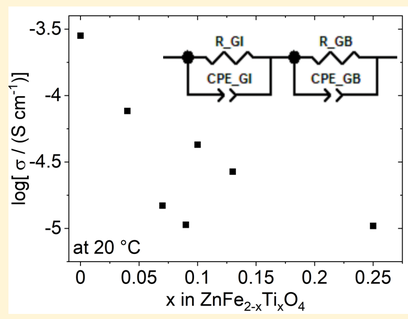
XRD measurements show a crystalline single phase material at x < 0.13.

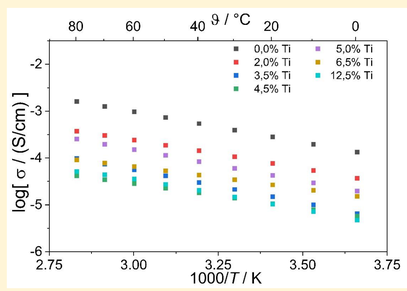
Average grain size but also standard deviation increase with increasing Ti addition.
The $ZnFe_2O_4$ samples with ethane diol (black) and butane diol (red) show comparable grain sizes within error of measurement.



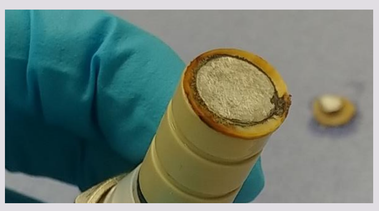
Electrochemical characterization pellets

Impedance spectroscopy measurements with ion blocking Pt contacts show that Ti addition lowers the electron conductivity with a local maximum around x=0.1, the pure sample has the best conductivity. Furthermore, the decreasing electron conductivity refutes the assumption that the Ti^{4+} doping leads to a donor doping. Electron conductivity is relatively high compared to other active materials.
First polarization-relaxation tests show a preliminary diffusion coefficient in range of $D_{chem}=2.4\cdot10^{-12} \pm 9\cdot10^{-13}$ cm^2 s^{-1} for $ZnFe_2O_4$.





Cell tests – aqueous electrolytes + Zn



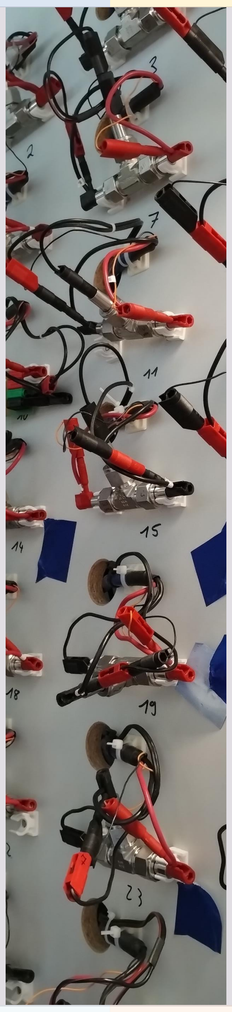
Cells with 3 M zinc triflate in water as electrolyte showed severe problems due to Fe leaching and subsequent low pH and gas evolution. In addition, Zn anode is having issues due to passivation layer development.

Countermeasure: Using Fe containing additives

$Fe(NO_3)_3$ → pH 1 → gas evolution and corrosion
$FeSO_4$ → formation and precipitation of $Fe(OH)_3$
$C_{12}H_{22}FeO_{14} \cdot 2\ H_2O$ → pH 2 → gas evolution and corrosion
Most other Fe salts not easily soluble in water.
Solution: Changing to an organic solvent.

Countermeasure: Try to clean passivation layer from Zn anode

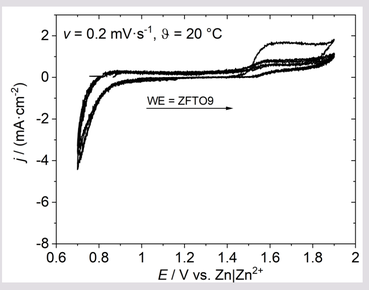
Polishing the metal foil → no effect
Polishing the metal foil in glovebox → no effect
Using electrochemically cleaned metal in glovebox → no effect
Solution: Changing to Sn as reliable anode.

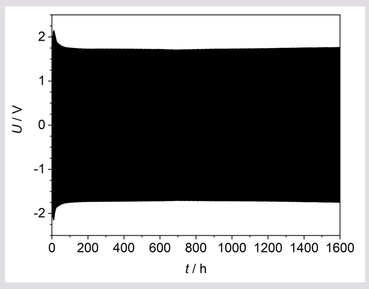


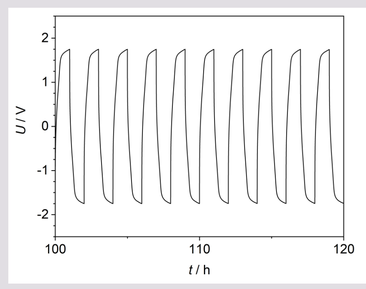
Cell tests – organic electrolyte + Sn

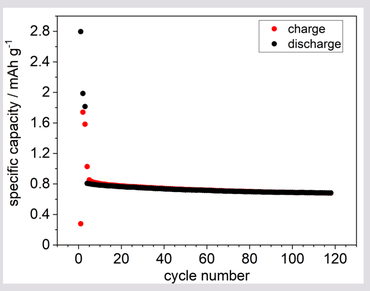
Spinel | 0.5 M zinc triflate in acetonitrile | Sn

Cells with organic electrolyte and tin as negative electrode show Zn ion (de)insertion with an oxidation peak at ~ 1.6 V and no clearly visible reduction peak.

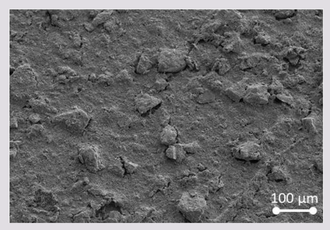








Symmetric cells with x=0.09 show stable cycling behavior over 800 cycles but high overpotential and low specific capacity → suboptimal particle morphology for electrode application



Conclusion & Outlook

$ZnFe_{2-x}Ti_xO_4$ was successfully synthesized using a Pechini synthesis route with x=0 to 0.25. The materials all showed high electronic conductivity and magnetic behavior. Calcined powders with x=0.09 as well as sintered powders without Ti-doping were successfully used as active material for the positive electrode with an organic electrolyte and Sn as negative electrode. For x=0.09, a stable cycling behavior over 800 cycles with 0.1 C and high overpotentials was found. At higher Ti concentrations no stable cycling behavior was observed.

Acknowledgements
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Literature:

[1] Bohra, Alman, Arras (2021) *Nanomaterials* 11 (5) 1286
[2] Morkhowa Rothenberger, Leisegang et al. (2021) *The Journal of Physical Chemistry C* 125, 17590-17533
[3] Liu, Rong, Malik et al. (2015) *Energy and Environmental Science* 8 (3) 964-974

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