Electrochemical Characterization of Ti-Doped Zinc Ferrite

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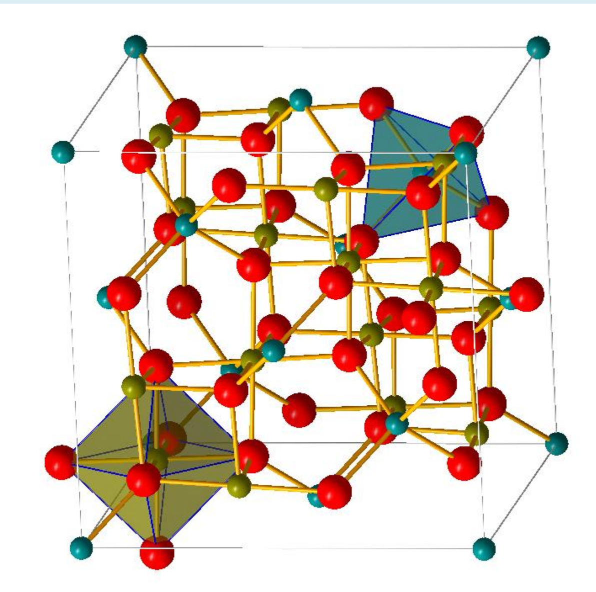
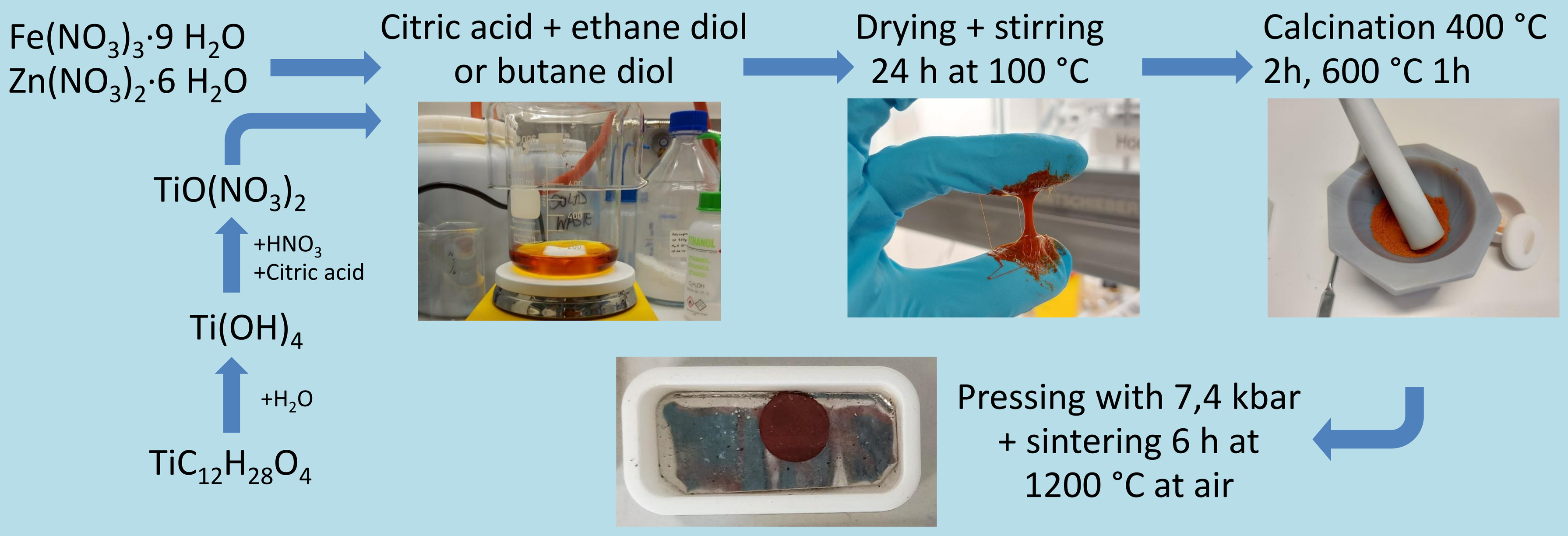
Material



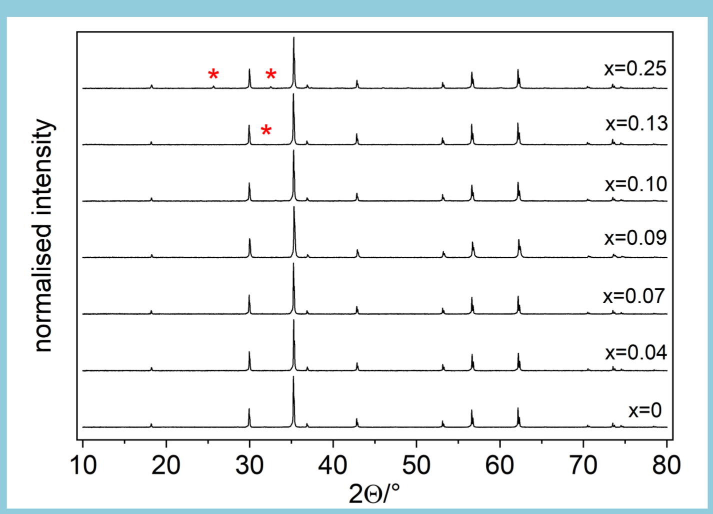
$ZnFe_2O_4$ is a well-known spinel material which is applied in a variety of areas ranging from anode material in lithium-ion batteries to photo-electrochemical water splitting and high-density magnetic data storage [1]. By doping with a tetravalent cation on the B position (Ti^{4+}), zinc vacancies 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 $ZnFe_{2-x}Ti_xO_4$

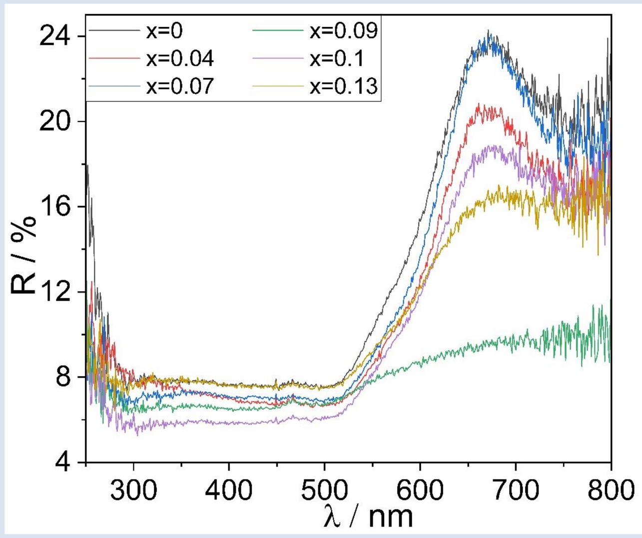


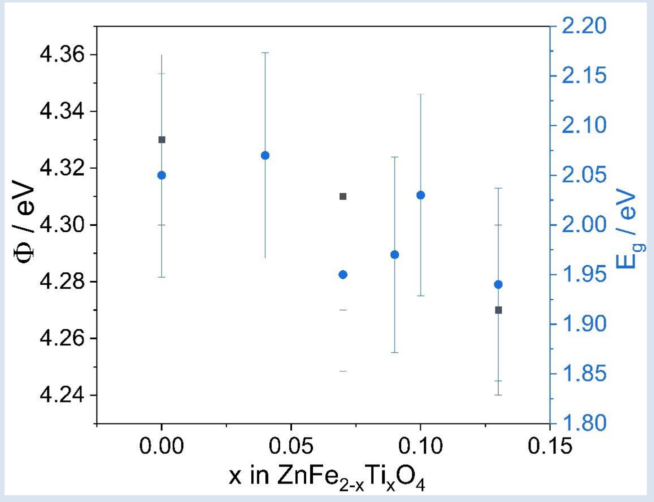
Structural analysis $ZnFe_{2-x}Ti_xO_4$



XRD measurements show a crystalline single phase at x<0.13, Rietveld refinement shows solubility limit for Ti^{4+} at 0.11 [4].

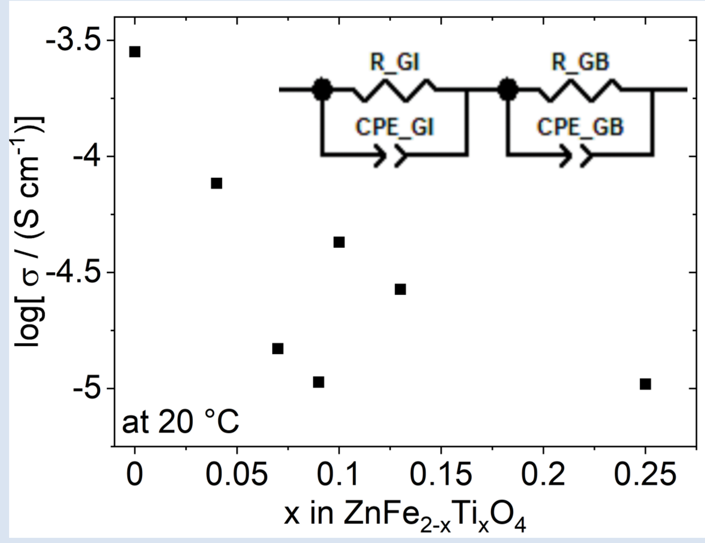
Optical and Electrochemical Characterization



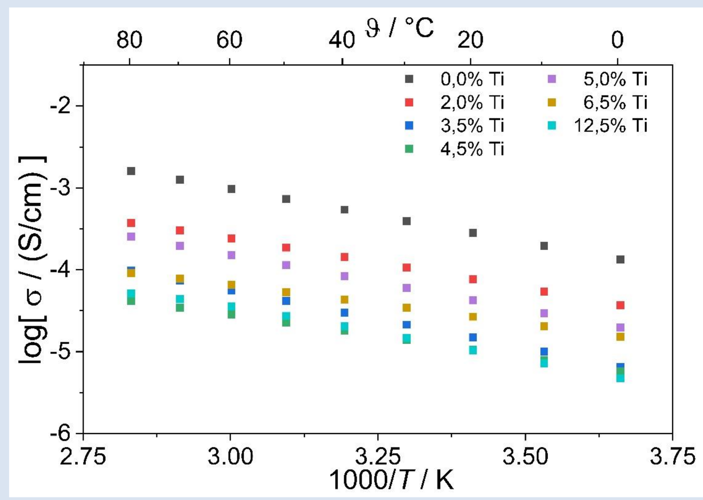


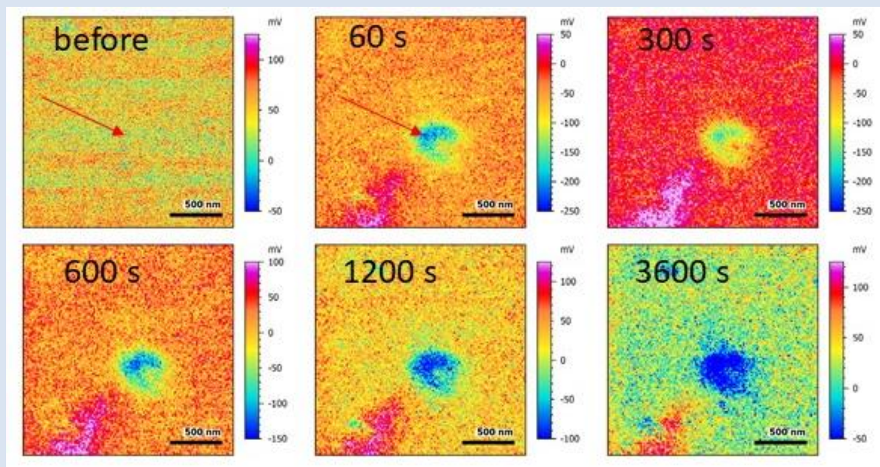
The diffuse reflection data of the grounded ceramics indicates that the Ti doping has a negligible effect on the optical band gap.

According to the turning point analysis, the band gap is located between 1.91 eV and 1.94 eV, except for x=0.09 which has a much higher band gap energy of 2.35 eV. This is probably due to an overstoichiometric amount of Zn [4].



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 [4].



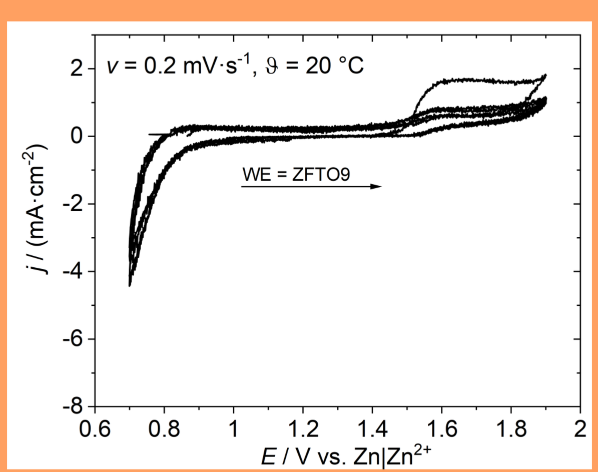


KPFM-based polarization-relaxation measurements (polarization -0.5 V for 60 s) find a chemical diffusion coefficient of $2.4 \cdot 10^{-12} \pm 9 \cdot 10^{-13}$ cm² s^{-1} for $ZnFe_2O_4$.

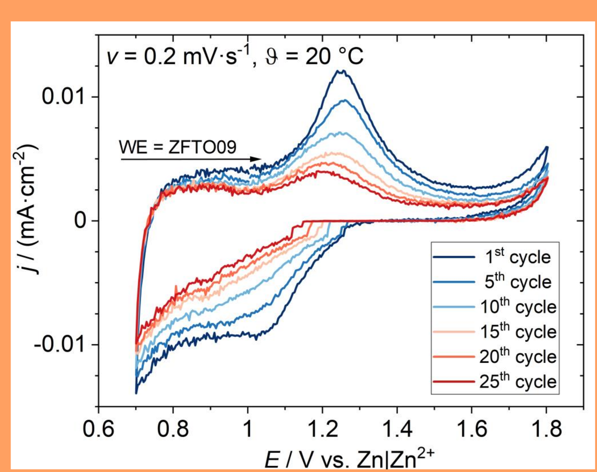
Cell tests – Electrolyte pH as key factor

Spinels show severe leaching of Fe^{3+} in aqueous electrolyte which leads to constant pH reduction of the electrolyte. Routes to reduce that issue are:

- Fe^{3+} salts as additives in electrolyte
- Using organic electrolyte (also higher potential)
- Using a commercial pH 5 buffer solution



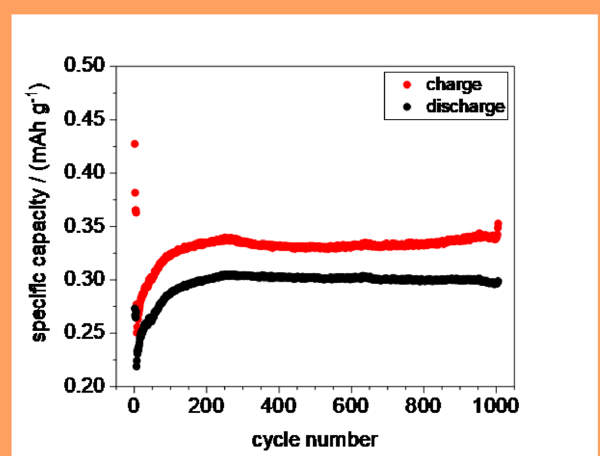
ZFTO09 | 3 M $ZnOTf_2$ (aq.) | Sn



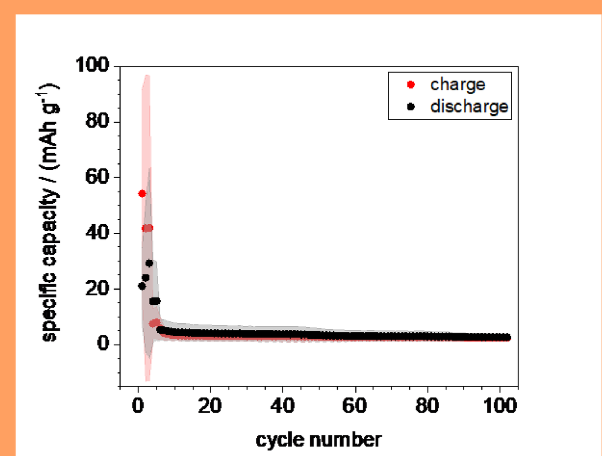
ZFTO09 | 3 M $ZnOTf_2$ in aq. buffer pH5 | Zn

Cell tests – Metal anode as key factor

- Sn foil could be easily implemented and showed results with all electrolytes, but cell voltage is severely lower (Sn: -0.141 V vs SHE, Zn -0.762 V vs SHE)
- Zn metal foil did not work with unbuffered aqueous electrolyte
- Sputtered Zn on Ti foil showed much higher capacities than Zn foil



ZFTO09|3 M $ZnOTf_2$ in acetonitrile | Zn
Zn metal sheet át 0.1 C



ZFTO09|3 M $ZnOTf_2$ in acetonitrile | Zn
Sputtered Zn on titanum foil át 0.1 C

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 comparably high electronic conductivity and magnetic behavior, but increasing Ti doping leads to a slight decrease of the work function and electronic conductivity.

If Fe leaching can be prevented, ZFTO can be used as active material with 1.25 V vs. Zn|Zn^{2+} with aqueous electrolyte and 1.57 V vs. Zn|Zn^{2+} with organic electrolyte (from CV). Further work will now encompass doping strategies to prevent leaching and optimization of particle morphology.

Acknowledgements
Patent pending on use of doped zinc ferrite as active material in zinc batteries. The authors thank Dr. D. Ensling for kelp with optical measurements and M. Holtkamp for help with µ-XRF measurement.

Literature:

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