Analysis of the Franklinite-Gahnite ($ZnFe_{2-x}Al_xO_4$) Solid Solution Series

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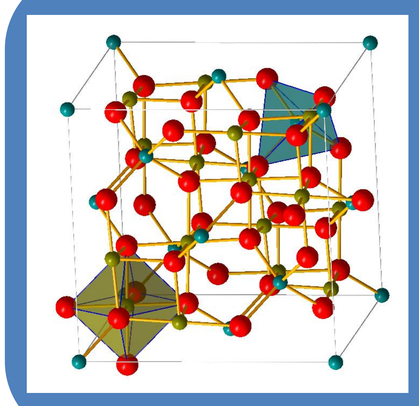


$ZnFe_2O_4$ is a well-known spinel material which is applied in a variety of areas ranging from anode material in lithium-ion batteries to photo-electrochemical water splitting and high-density magnetic data storage [1], but it can also be applied at the cathode in zinc batteries. By doping with a non-redoxactive cation on the B position (Al^{3+}), we tried to improve cycling stability and prevent Fe leaching in contact to aqueous electrolytes.

$Fe(NO_3)_3 \cdot 9\ H_2O$
$Al(NO_3)_3 \cdot 9\ H_2O$
$Zn(NO_3)_2 \cdot 6\ H_2O$

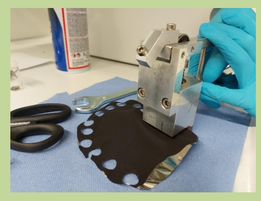
Citric acid + butane diol

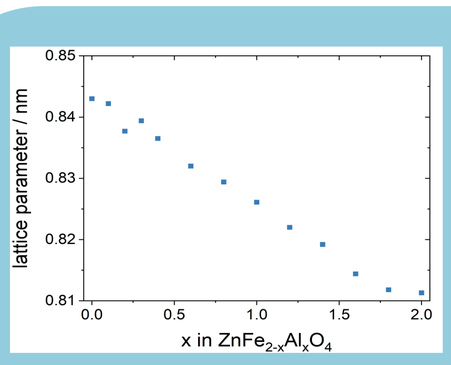
Drying + stirring 24 h at 100 °C

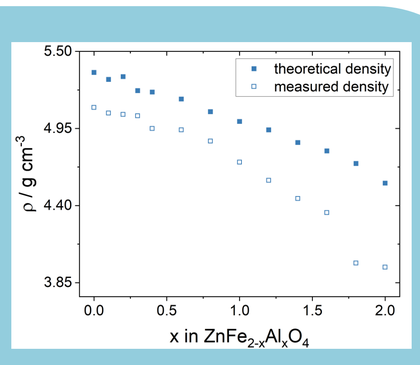
Calcination 400 °C 2h, 600 °C 1h

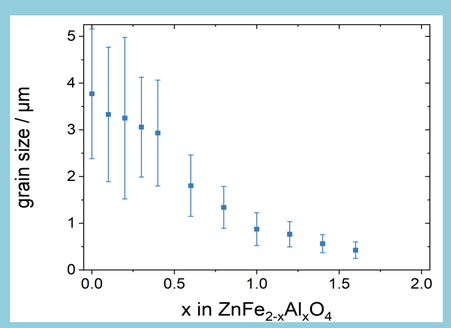
Materials analysis with sintered ceramics

Cell analysis with as-received powders



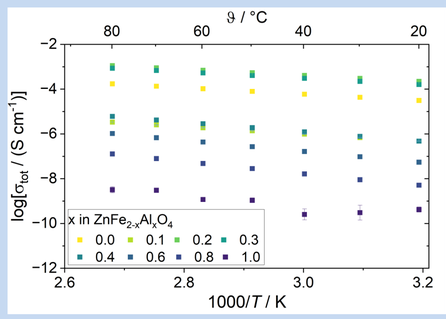


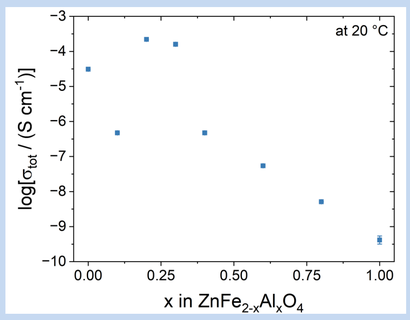


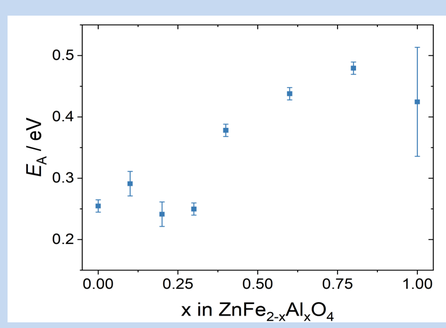


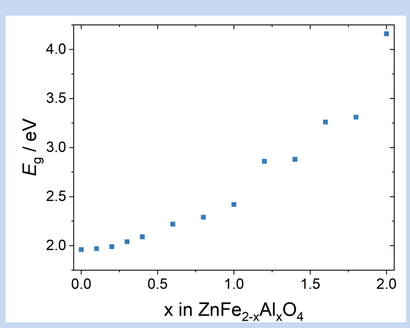
- Single phase material
- Lattice parameter decreases with $[Al^{3+}]$
- Density and grains size depends strongly on Al concentration

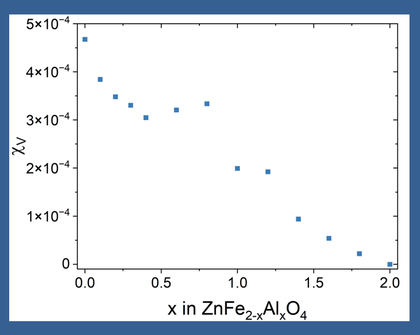
Highest total conductivity, lowest activation energy and low optical band gap for materials with $0.1 \leq x \leq 0.3$.



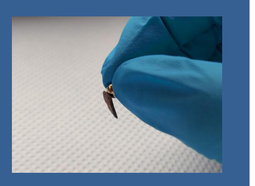


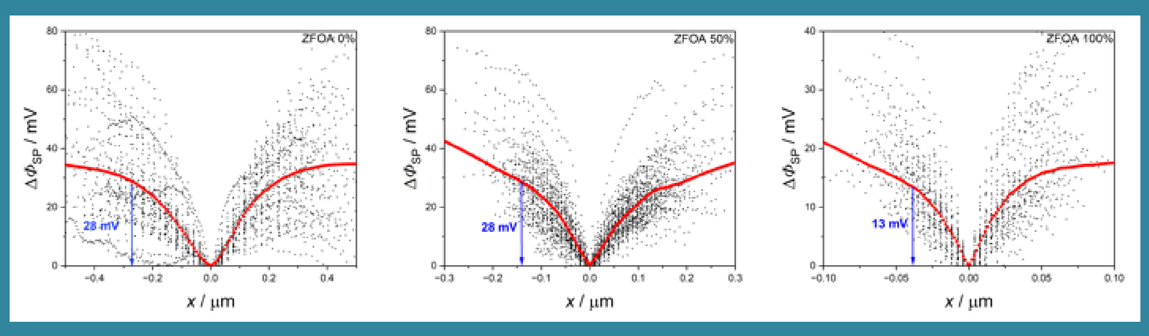




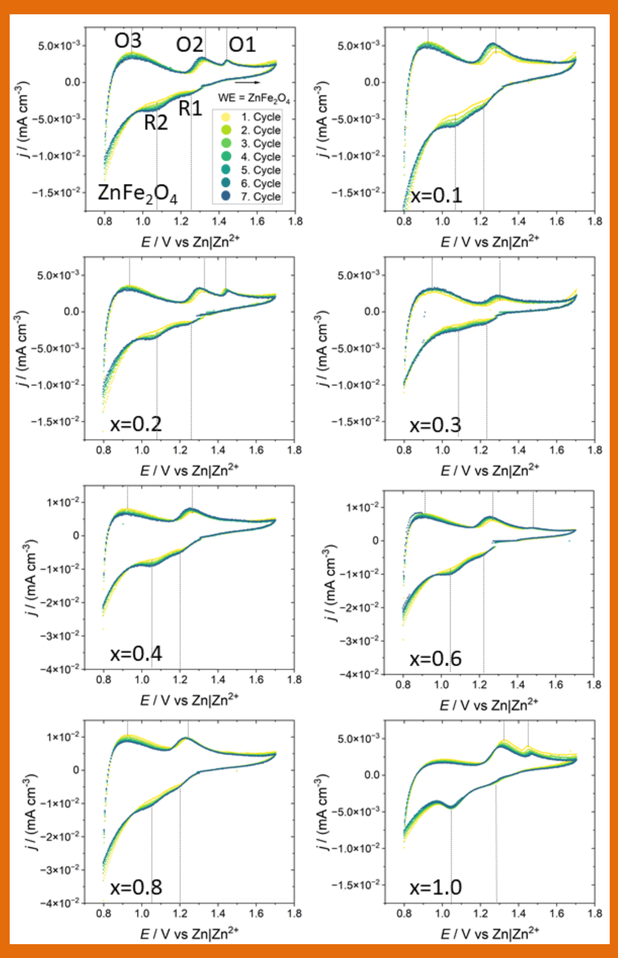


Magnetic properties change strongly: pure Gahnite is diamagnetic, pure Franklinite can be picked up with a magnet





AFM measurements in accordance to impedance spectroscopy measurements show that Al concentration does not affect the potential barrier at the grain boundaries



All materials up to x=1.0 show reversible Zn^{2+} (de)insertion (O2/R2) and additionally more or less pronounced proton (de)insertion (O1/R1).

Cells: Spinel||zinc foil with 3M $Zn(OTf)_2$ in pH 5 buffer solution.

Conclusion & Outlook

The full solid solution series $ZnFe_{2-x}Al_xO_4$ was successfully synthesized using a Pechini synthesis route. Materials with $0.1 \leq x \leq 0.3$ show a promising combination of high electronic and ionic conductivity and are able to reversibly (de)insert zinc ions and protons.
Future work will be carried out to cycle the materials with improved zinc electrodes, since the currently achieved specific capacities are very low due to dendrite formation and parasitic reactions at the negative electrode.

Literature:
Krämer, Hopster, Windmüller et al. *Energ. Adv.* **3** (2024) 2175-2185 DOI: 10.1039/D4YA00134F

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