XES Nanoprobe for Hard X-Ray Region: Mitigating Degradation in Ni-ZEBRA Batteries

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Purpose

- Improve scientific understanding of link between Ni-$NiCl_2$ ZEBRA battery cycle degradation and FeS additive
- Chemical and morphological imaging at hierarchical length scales, focusing on development of X-ray Emission Spectroscopy Mapping (XESM).

Key Successes

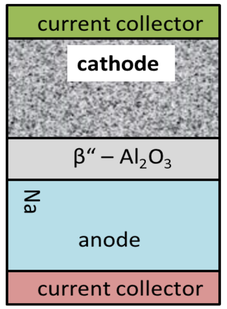
- 1% FeS optimally improved battery performance by poisoning Ni surfaces – optimizing Ni/NiCl2 distributions and conductive pathways
- This change in surface reactivity leads to a marked effect on heterogeneity over different scales that impacts battery degradation.

Research Accomplishments

mm → Length scale/resolution → nm

Ni-ZEBRA Battery

We examined Ni ZEBRA cathodes in the charged state to understand how FeS prevents capacity degradation with cycling



Overall reaction

$2NaCl + Ni \leftrightarrow NiCl_2 + 2Na$

Discharged Charged

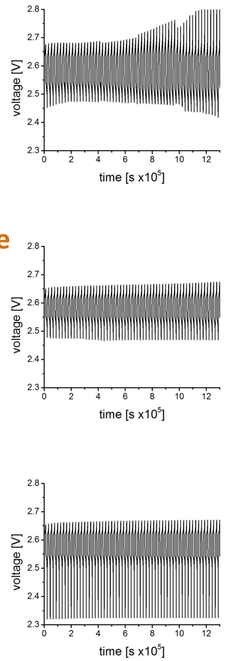
E_0 = 2.58 V at 300°C

The cathode contains additional Ni than indicated by this reaction to provide electrical connectivity. Molten $NaAlCl_4$ in the cathode provides Na^+ conductivity

0.01 % → FeS Additive → 1 % → 2 %

Battery performance (PNNL)

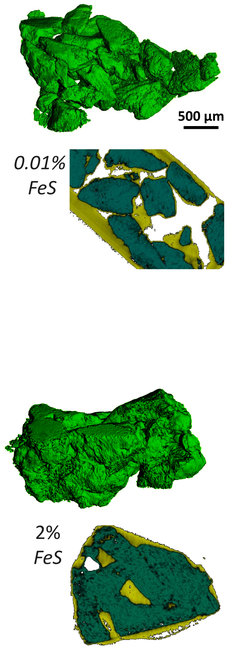
Voltage over 60 (dis)charge cycles



1% FeS additive yields optimum battery performance—prevents breakdown seen in 0.01% FeS sample

X-ray tomography (PNNL)

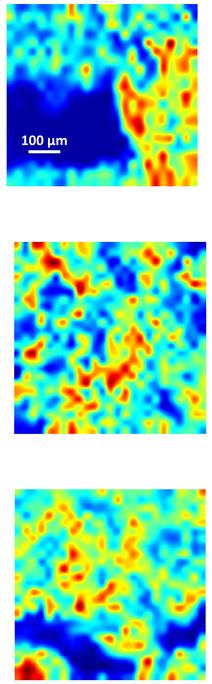
Absorption contrast through entire cathode thickness



FeS additive improves conductive pathway of the Ni-rich (green) regions through electrolyte (yellow)

X-Ray fluorescence (APS)

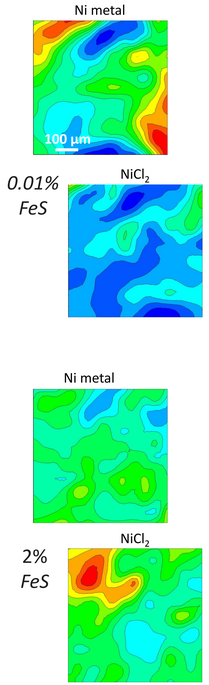
Provides elemental concentration of Ni



This connectivity is present even at much finer length scales, optimized at 1% FeS

Micro-XRD (PNNL)

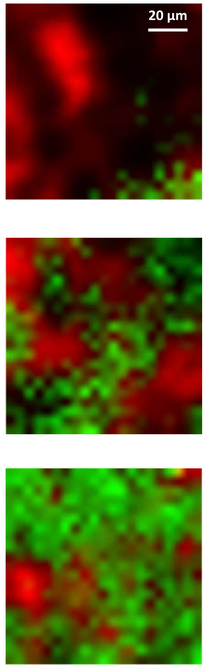
Phase identification, 50-µm spot size



Higher FeS concentrations lead to more homogeneous Ni/$NiCl_2$ distribution

XES maps (PNNL)

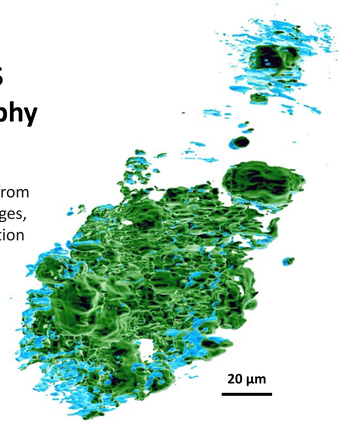
Speciation of Ni from deconvolution of XES spectra at 5-µm resolution



1 % FeS shows optimum mixing and connectivity of Ni (red) and $NiCl_2$ (green)

XANES tomography (SSRL)

Elemental identification from absorption edges, <1-µm resolution



Fe (blue) migrates to the grain boundaries of Ni (green) particles

Publications

- Bowden ME et al. 2014. *J. Power Sources* 247:517
- Mortensen DR et al. 2013. *Rev. Sci. Instr.* 84(8):083908
- Alvine KJ et al. 2014. *Appl. Phys. Lett.* (to be submitted)

Next Steps

- Beam time at SSRL July 2014 to map sulfur and complete tomography
- *APL* and *Adv. Energy Mat.* manuscripts in preparation
- Pursuing external funding through DOE/OVT and DOE/EM in related XESM applications