SAND2022-11214C

Sandia National Laboratories

Exceptional service in the national interest

Microwave Synthesis of FeF_2@C Composites as Conversion Cathodes for Li Metal Batteries

Bryan R. Wygant, Noah B. Schorr, Igor V. Kolesnichenko, Timothy N. Lambert

Sandia National Laboratories, Albuquerque, NM

American Chemical Society Fall Meeting 2022

ENFL 3731641

Chicago, IL

August 23, 2022

SAND# Here

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. ...ation under contract DE-NA0003525.

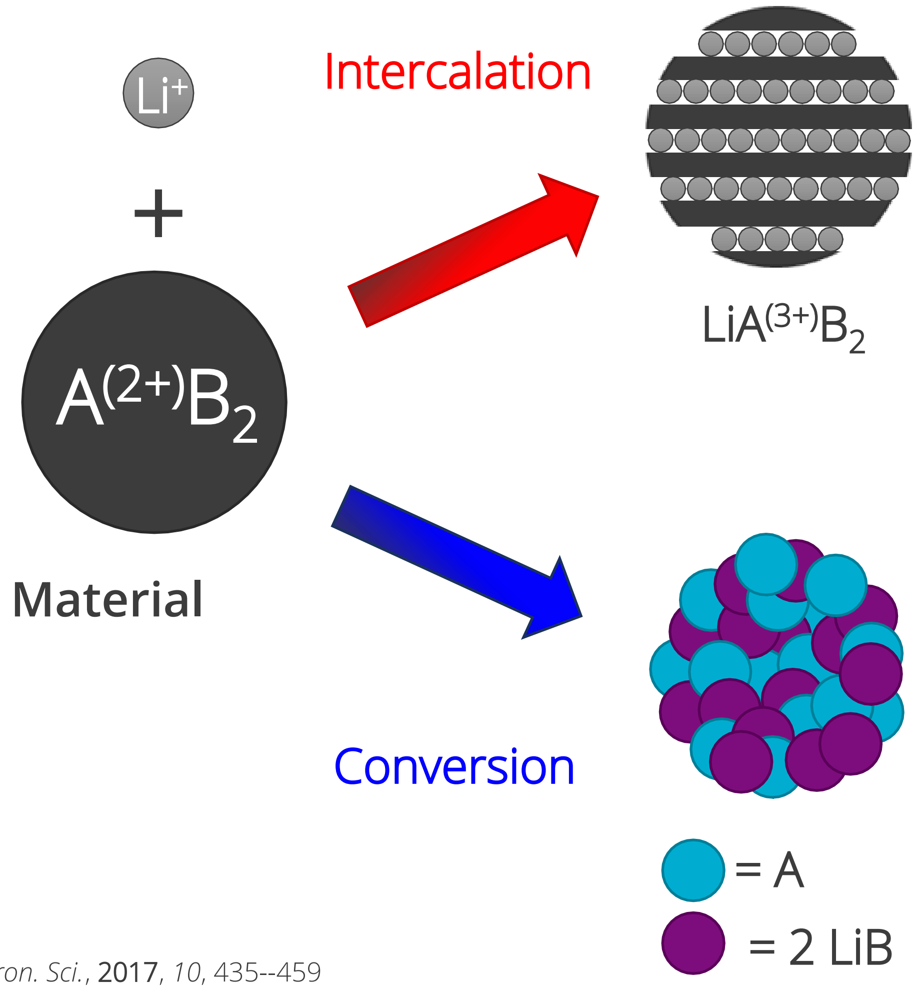
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

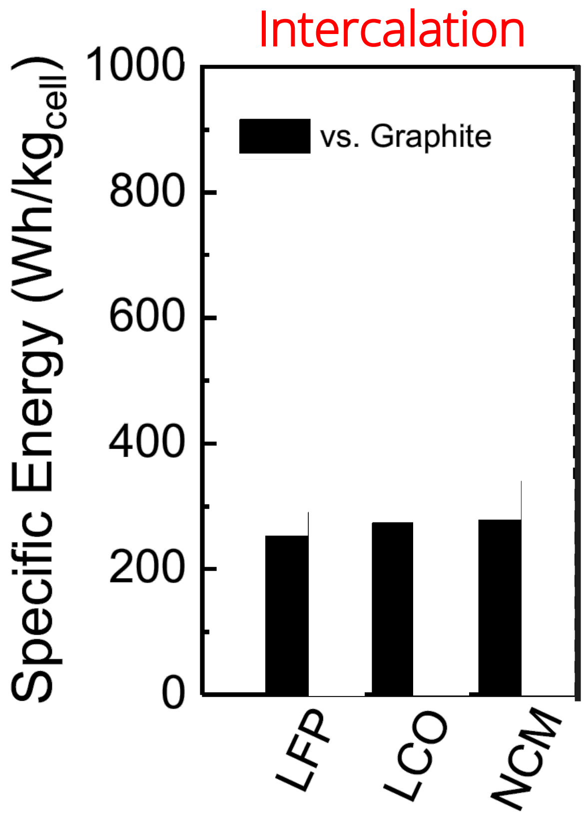
U.S. DEPARTMENT OF ENERGY

NNSA

Conversion cathodes to enable Li metal batteries

- Moving beyond Li-ion batteries requires both Li metal anodes *and* compatible, high-capacity cathodes

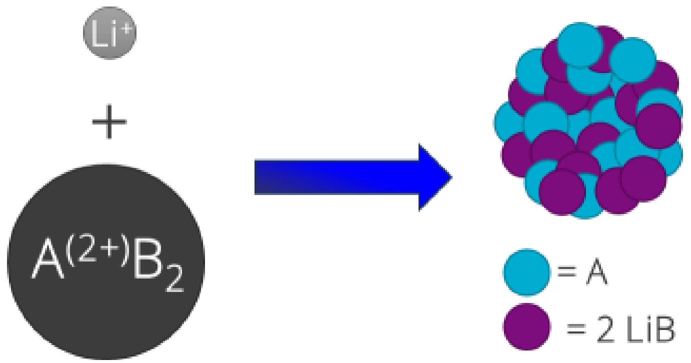




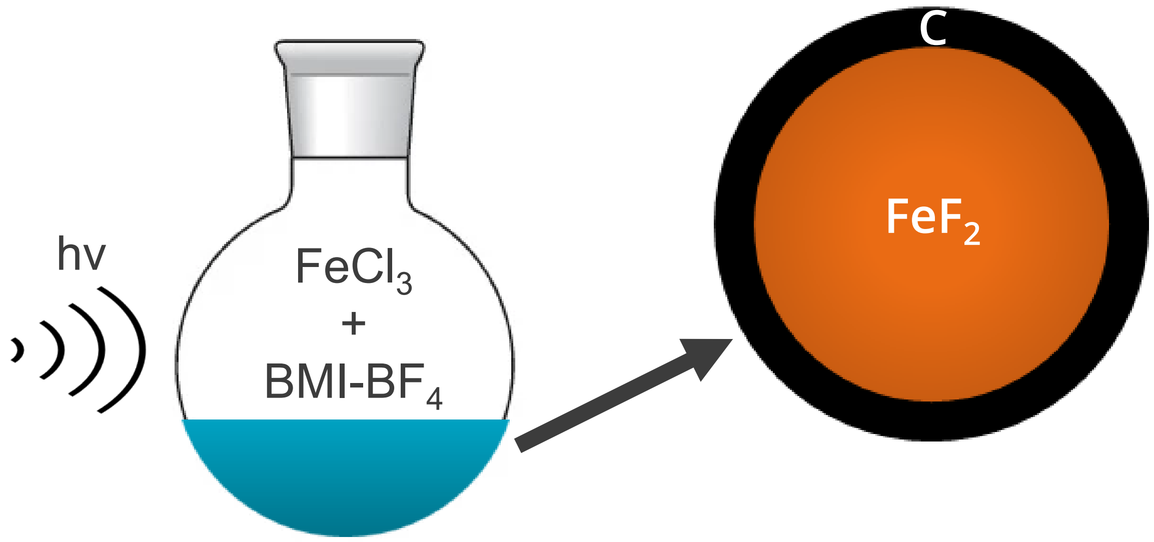
Wu *et al. Energy Environ. Sci.*, 2017, *10*, 435--459

Overcoming Challenges of Conversion Cathodes

- Despite promise of higher capacity, higher energy density batteries, conversion cathodes suffer from limitations
  - Irreversibility/low conductivity (CF_x, LiF)
  - Side reactions (polysulfides, electrolyte degradation)
  - Slow reaction kinetics
- How do you overcome these challenges?



- Microwave synthesis to produce C-coated, nanoparticulate FeF_2 that shows good performance when paired with Li metal
  - Conductive shell, Fe protected from electrolyte, improved Li transfer to FeF_2

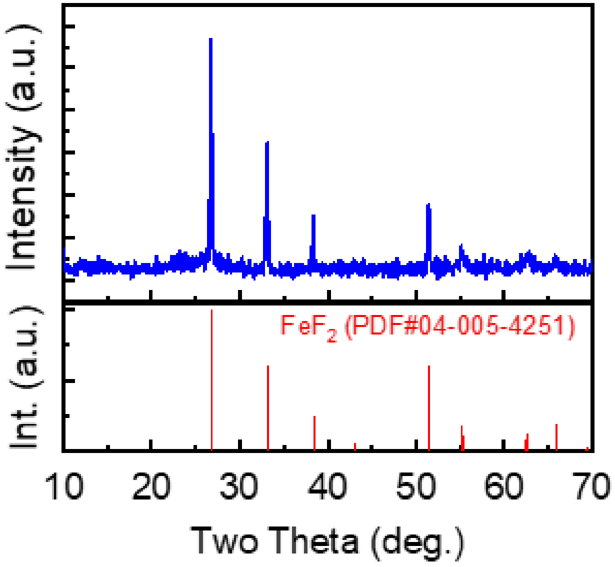


Jacob *et al.*, *Chem. Mater.* **2006,** *18*, 3162-3168

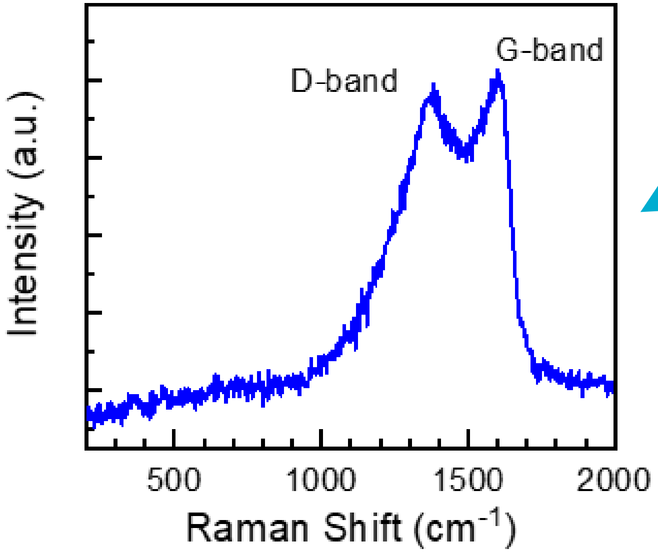
$BMI\text{-}BF_4$ = 1-butyl-3-methylimidazolium tetrafluoroborate

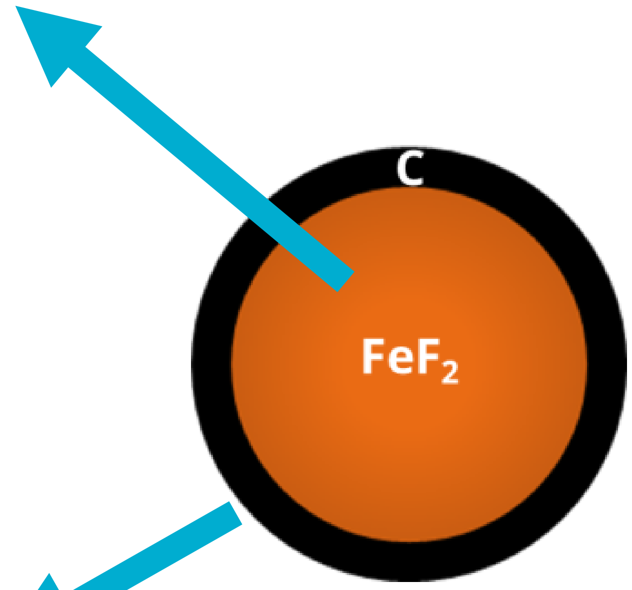
Characterization shows successful synthesis of FeF_2@C

XRD



Raman

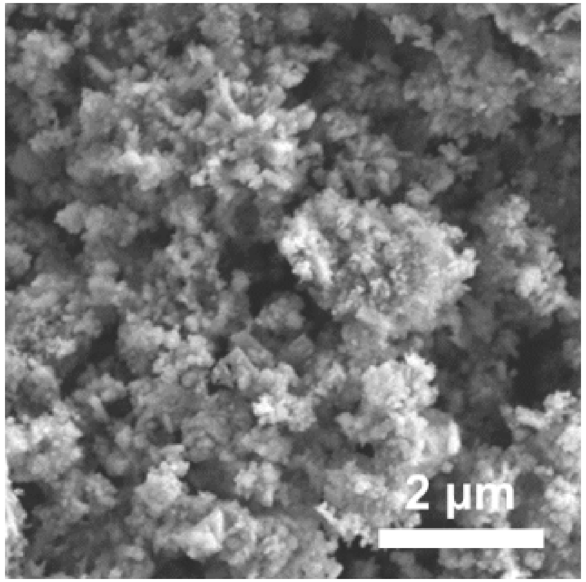


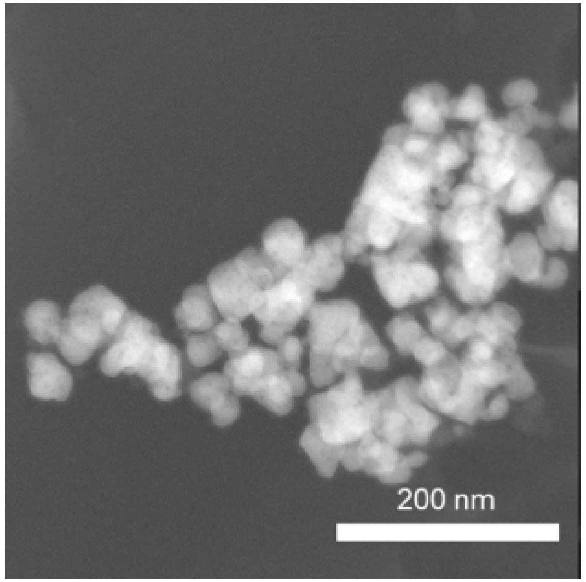


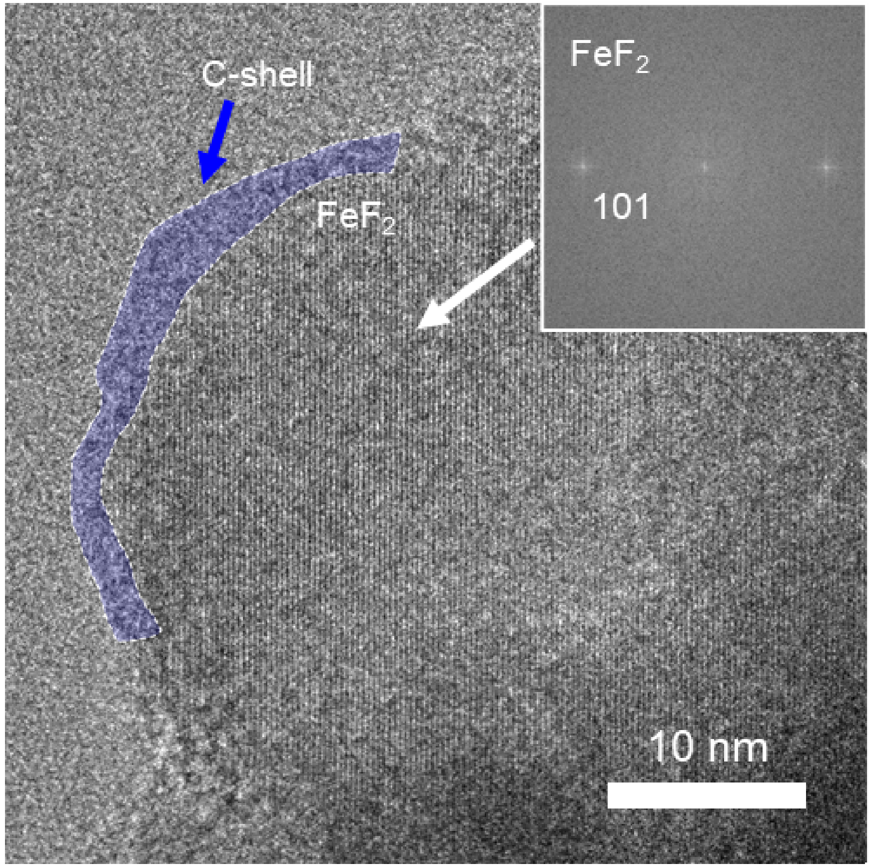
- XRD confirms phase-pure, crystalline FeF_2 is formed during synthesis
  - No oxides, hydroxides, metal

- Raman spectroscopy shows presence of partially amorphous carbon in material
  - I_d/I_g ratio of 0.96 suggests > 10 Å clusters of aromatic carbon

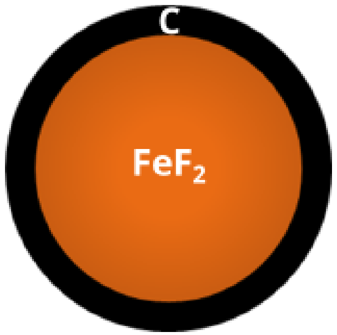
Electron microscopy confirms presence of C shell







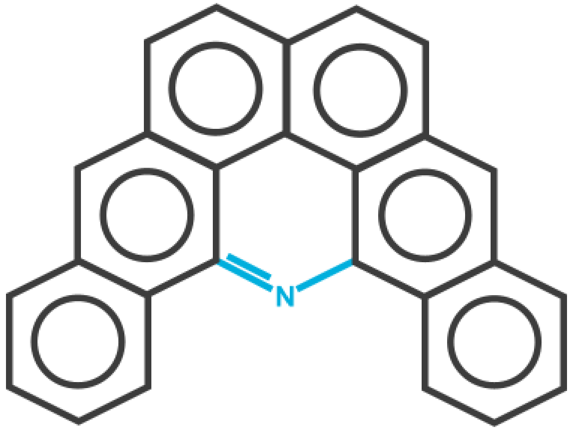
- SEM allows us to see the FeF_2@C powder is composed of agglomerations of sub-micron particles
  - STEM shows these particles are 35 -100 nm in diameter
- HRTEM images confirm presence of thin (2-3 nm) layer of carbon on the surface of the particles

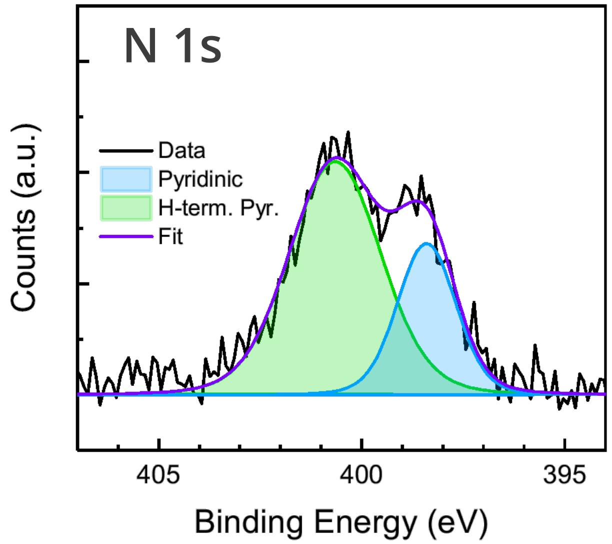


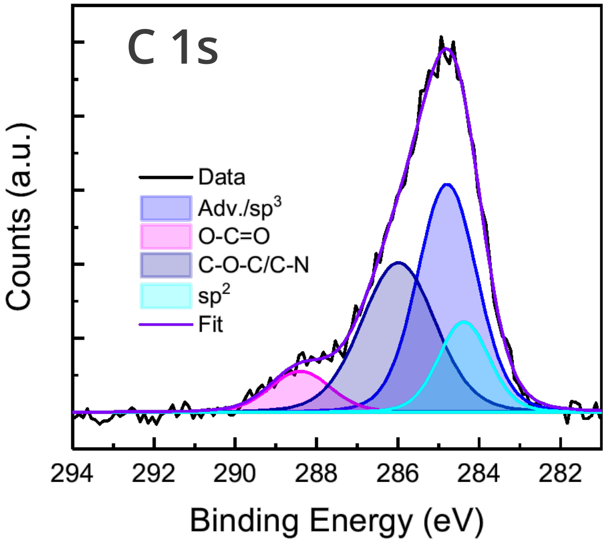
Elemental and chemical composition of FeF_2@C and Shell

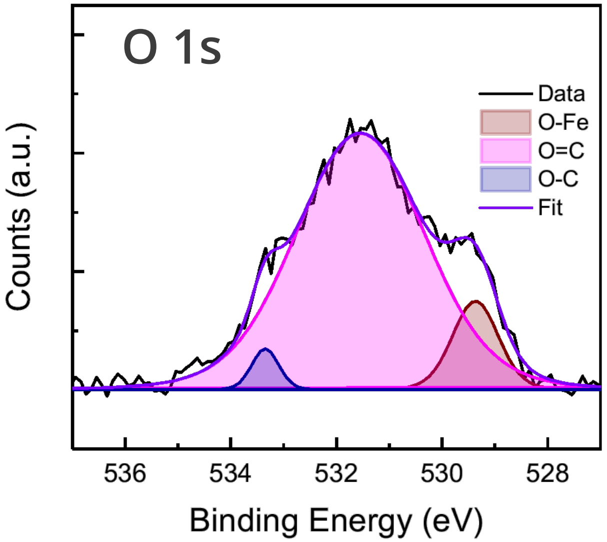
- Elemental analysis confirms C-shell represents a small portion of the mass of the FeF_2@C material (~7.2% by mass)

- X-ray photoelectron spectroscopy (XPS) provides evidence for:
    - Pyridinic N moieties in the C-shell
    - sp^2 and sp^3 carbon
    - Oxidized carbon species
    - Fe-O (oxidized FeF_2 surface)



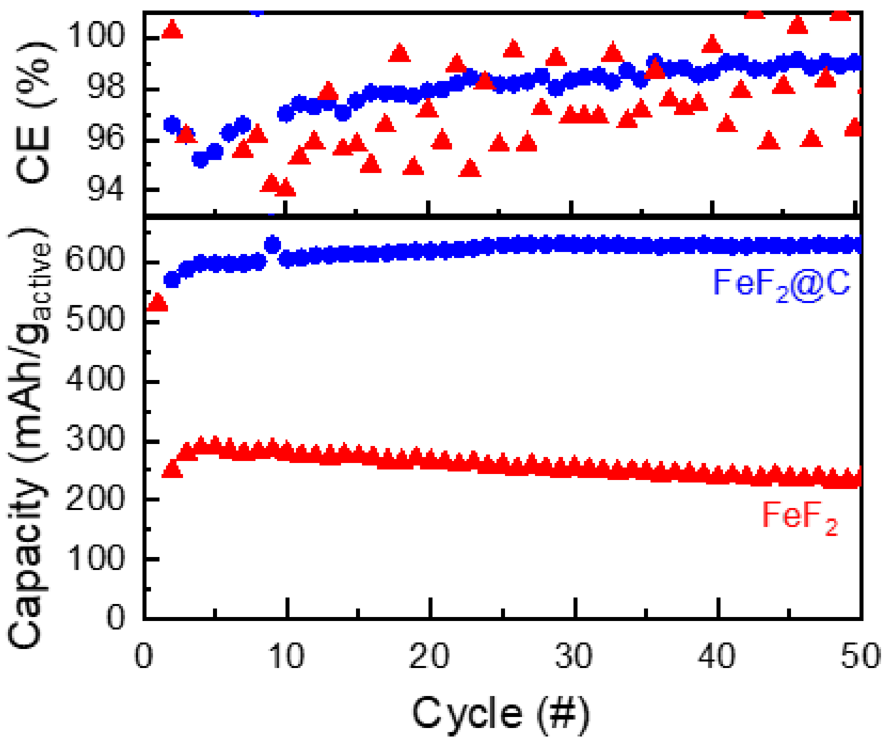




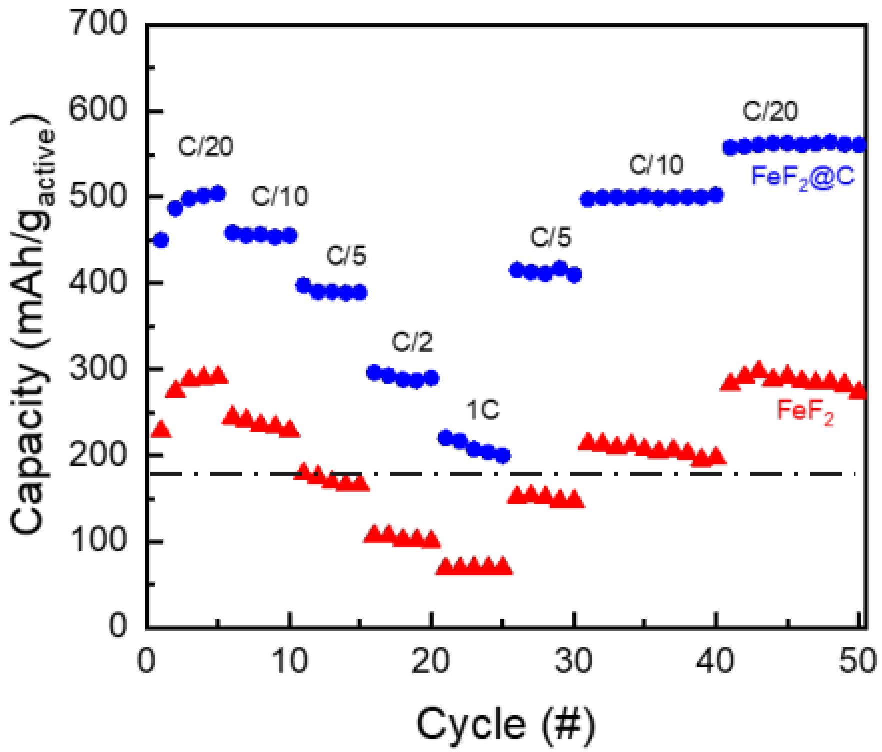


FeF_2@C shows excellent cycling performance in Li metal battery

- Tested vs. Li anode @ C/20, the FeF_2@C cathode shows excellent performance vs. comparable commercial FeF_2 cathode
  - > 300 mAh/g higher capacity than FeF_2
  - Minimal capacity loss over 50 cycles (1-4V)
  - More consistent CE, building to 99%

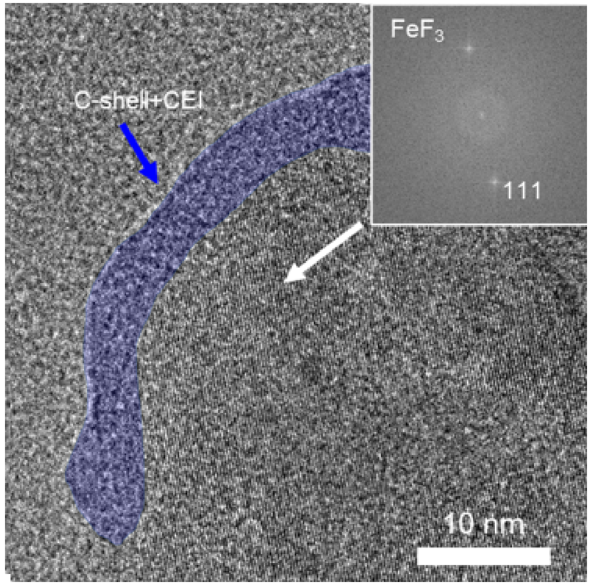


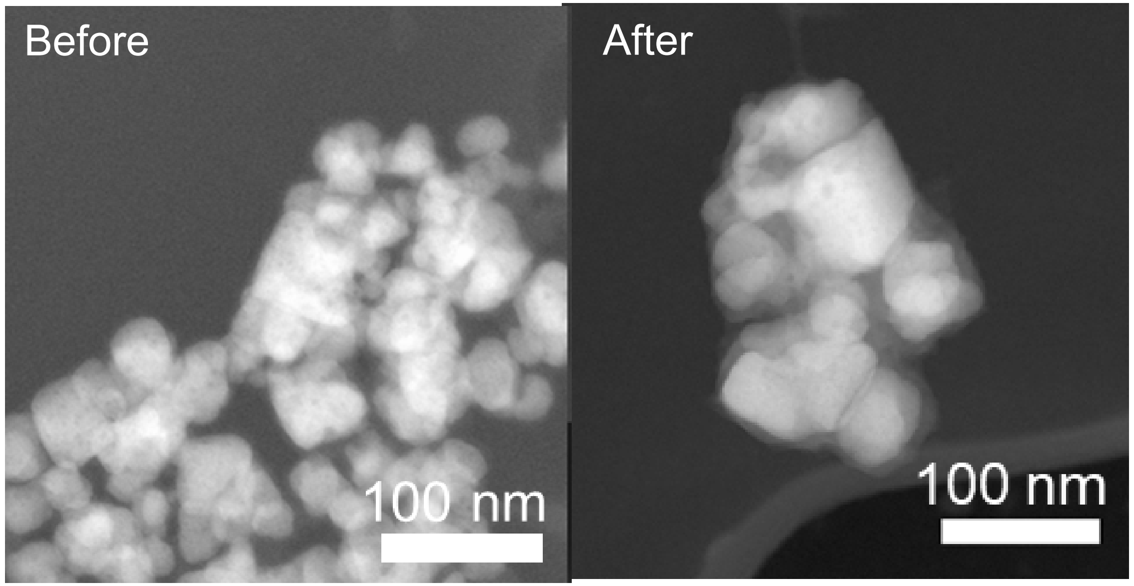
- FeF_2@C also shows better rate cycling performance, even at rates as fast as 1C
  - Minimal loss in capacity even after cycling at high rates
  - ~200 mAh/g capacity at 1C vs. 170 mAh/g theoretical capacity of LFP

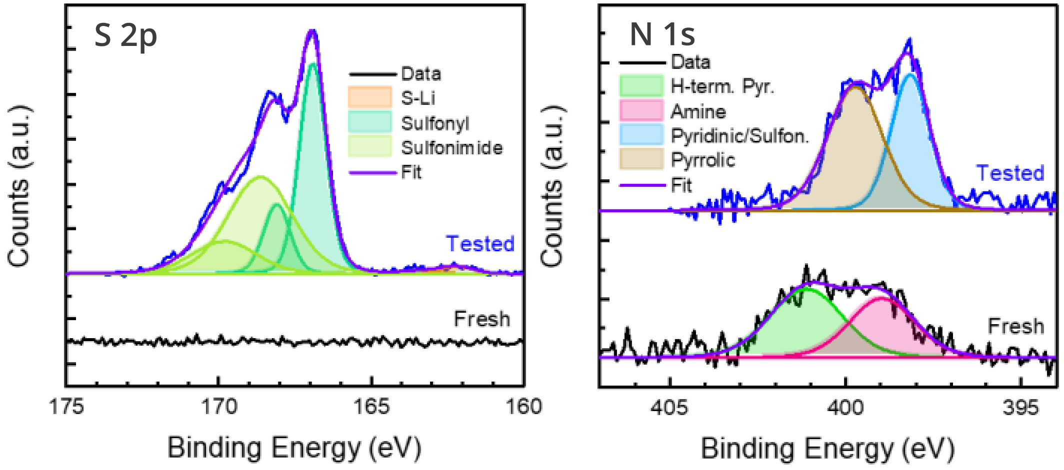


$LiFePO_4$
170 mAh/g

Carbon Shell and CEI present after cycling



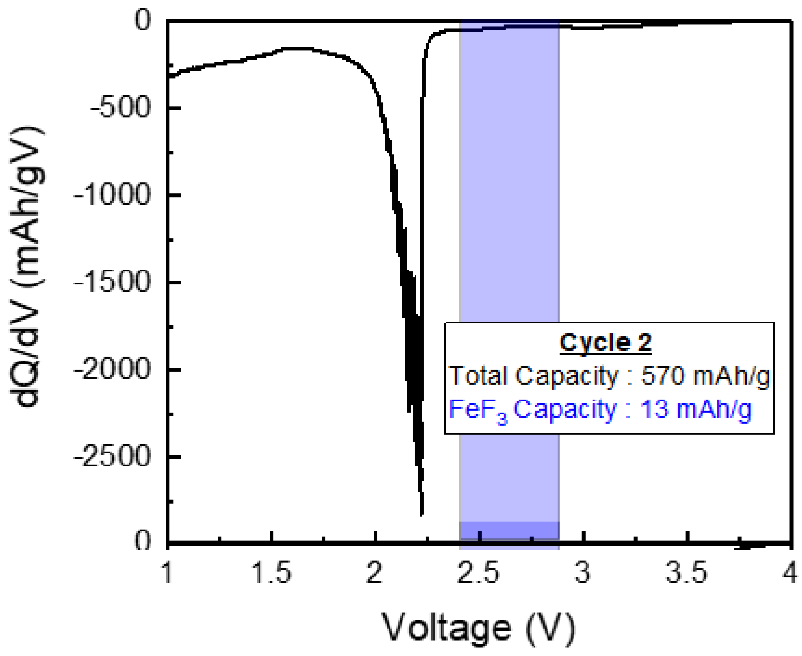


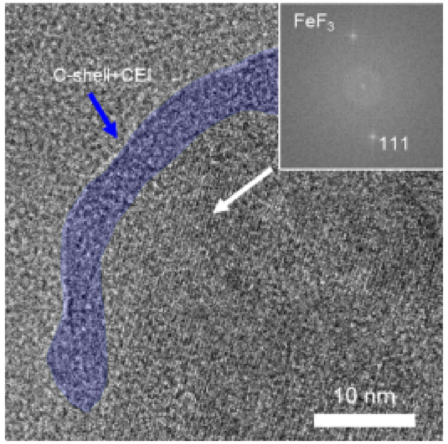


- HRTEM and XPS confirm the growth of a ~ 2 nm CEI layer atop the C-shell
  - FSI^- derived CEI species on surface
  - SAED indicates presence of FeF_3 after cycling
- Similar particle sizes before/after cycling *via* STEM

FeF_3 formation allows for higher capacity

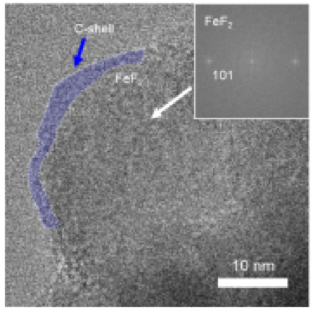
- Analysis *via* SAED and dQ/dV both indicate presence of FeF_3
- Formation and cycling of FeF_3 (712 mAh/g) helps explain extra capacity observed in FeF_2@C
  - Likely protected by C-shell, preventing deleterious side reactions

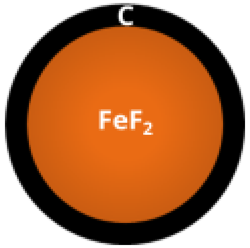


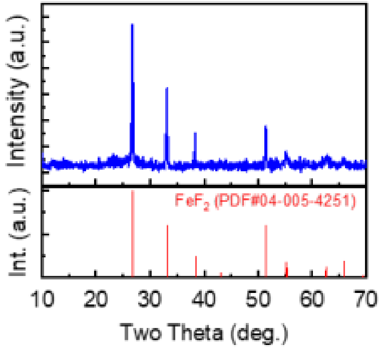


Summary

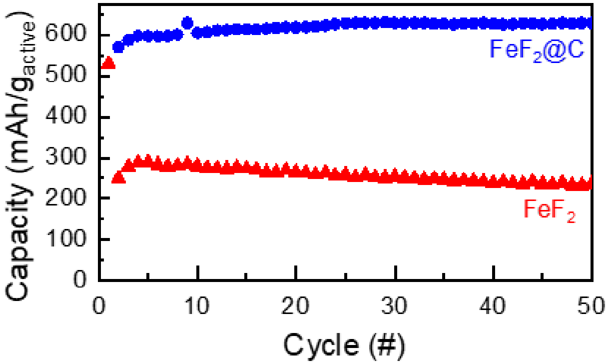
1. Microwave synthesis of phase-pure FeF_2 surrounded by thin carbon shell (FeF_2@C)



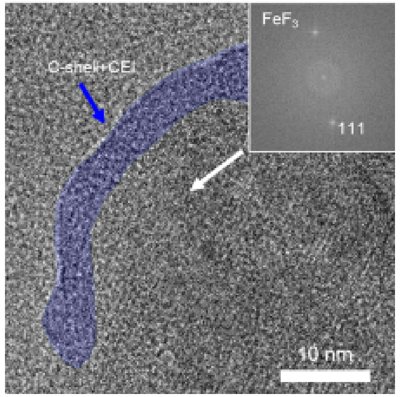




2. Demonstrates excellent cycling performance relative to commercial FeF_2 cathodes



3. C-shell and CEI appear to protect FeF_2 surface after cycling with thin (4-5 nm) surface layer, while FeF_3 adds additional capacity



Acknowledgements

- *Mentors*
  - Dr. Tim Lambert and Dr. Katie Harrison
- *Co-Authors*
  - Dr. Noah Schorr
  - Dr. Igor Kolesnichenko
- *Experimental Data Collection*
  - Sara Dickens (SEM)
  - Dr. Paul Kotula (STEM)
  - Dr. Samantha Rosenberg (XPS)
- *Funding*
  - Sandia National Laboratories LDRD Program


Tim Lambert


Katie Harrison


Igor Kolesnichenko


Noah Schorr

Sandia National Laboratories

LDRD Laboratory Directed Research and Development

THIS WORK WAS SUPPORTED THROUGH THE SANDIA LDRD PROGRAM

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Thank you for your attention!