Cutting Out Cobalt: Cathode Alternatives

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ENMA 650 Final Project

Presentation Outline

I. Problem Area & Background

II. Challenges of Cobalt Alternatives

III. Solution & Scientific Analysis

IV. Research Approach Details

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I. **Problem Area & Background**

II. Challenges of Cobalt Alternatives

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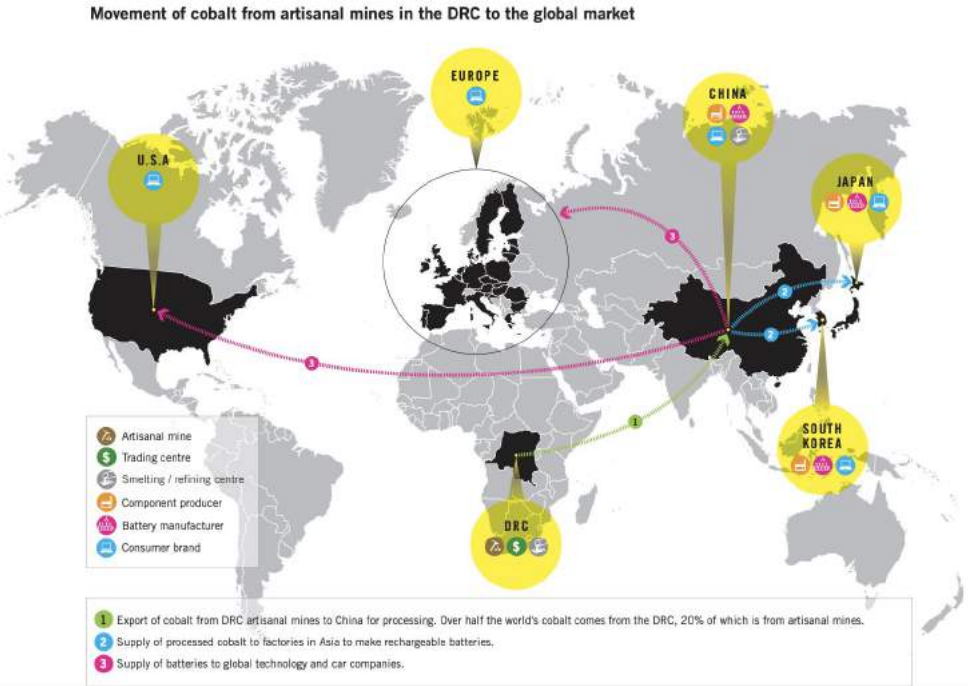
Elemental Abundance

- ~0.003% of Earth's crust
- Mining byproduct of nickel or copper
- Demand to double by 2030

Geographic Areas

- Democratic Republic of the Congo (DRC)
  - ~70% world supply
- Additional zones



ckground

Functions for Society

- Electronics market
  - Largest importer - China
- Electric vehicles market

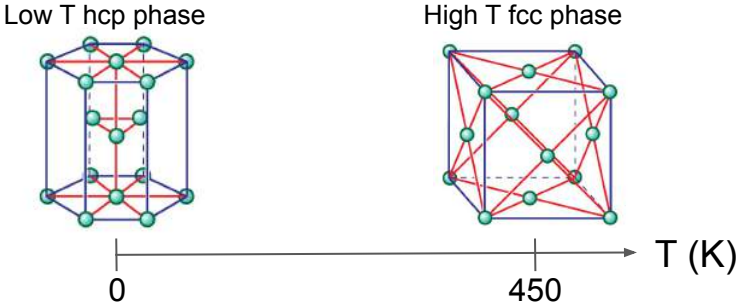
Graphic: Amnesty International

Cobalt Properties

- Basic properties
  - Brittle
  - Ferromagnetic
  - High melting point
  - High corrosion resistance

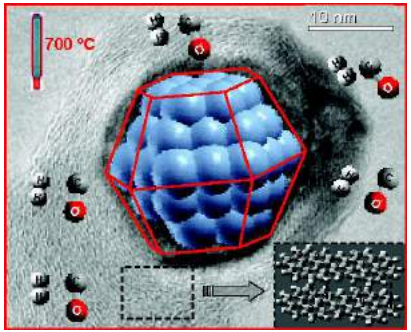
Heterogenite

Photo: Rob Lavinsky



- Mechanical processes cause crystal transformations
  - Milling enhances properties
  - Additives and nanoconfinement can stabilize crystal phases in less favorable conditions

High T stabilization of hcp phase



Chem. Mater. 2009, 21, 23, 5637–5643

Applications of Cobalt

- Cathodes for rechargeable batteries
  - Layered $LiCoO_2$ intercalates in lithium ion batteries
- Biomaterials for joint replacement
  - Corrosion and wear resistance of alloys
- Gas turbines in aerospace engineering
  - High temperature strength of alloys

Photo: Sanjay Acharya

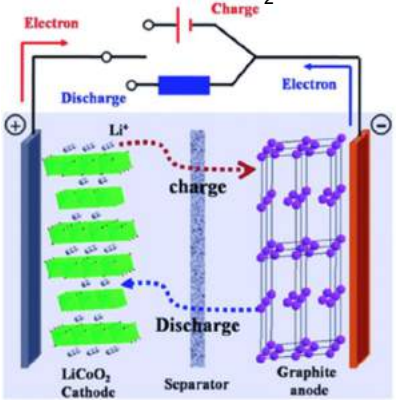
Home Depot

Biomaterials and Applications 2019, 4, 199-287

Selected Application: Lithium Ion Batteries

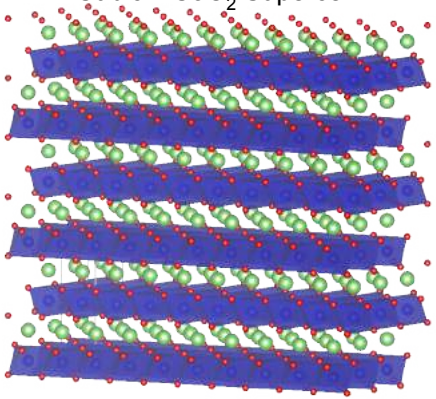
- $LiCoO_2$ is most common cathode material in rechargeable lithium ion batteries (~70% world's cobalt use)
- Layered cobalt oxide structure allows for intercalation of lithium, enabling high cycling stability

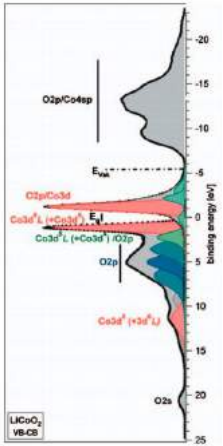
Schematic of $LiCoO_2$ Battery



Royal Chemistry Society

Cubic $LiCoO_2$ Supercell





$LiCoO_2$ has a small band gap, critical for the electron transfer in the cathode.

Potential replacements need to have comparable electron transfer capabilities

D. Ensling, A. Thissen, S. Laubach, P. C. Schmidt and W. Jaegermann, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 82, 195431.

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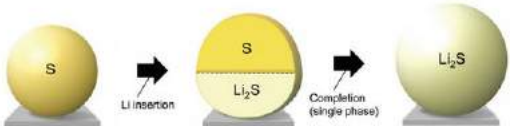
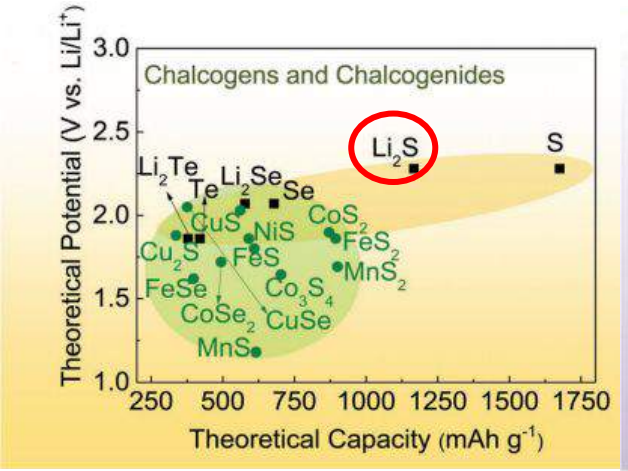
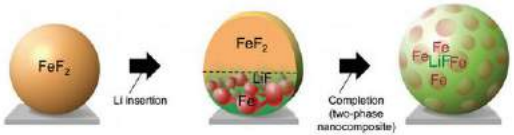
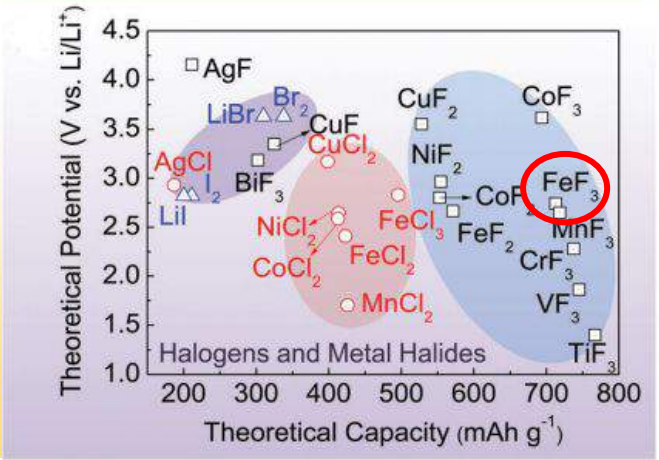
Conversion Cathodes





LiS:
0.042 % S in Earth's Crust





FeFx:
0.054 % F in Earth's Crust
6.3 % Fe in Earth's Crust

Li ions bond to cathode material instead of intercalation between layers

- Wide range of reactions possible
- More than one Li ion per metal
- Sustainable materials available

Energy Environ. Sci., 2017, **10**, 435

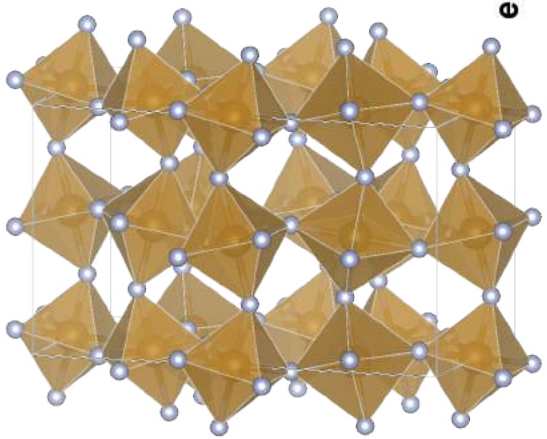
FeF_3 Structure & Bandgap

- Different computational techniques give band gaps in the range 2.5 - 6.0 eV
  - Not great for a potential cathode material
- This can be modified in a few ways:
  - Nanoconfinement in a conducting medium
  - Introduction of dopants

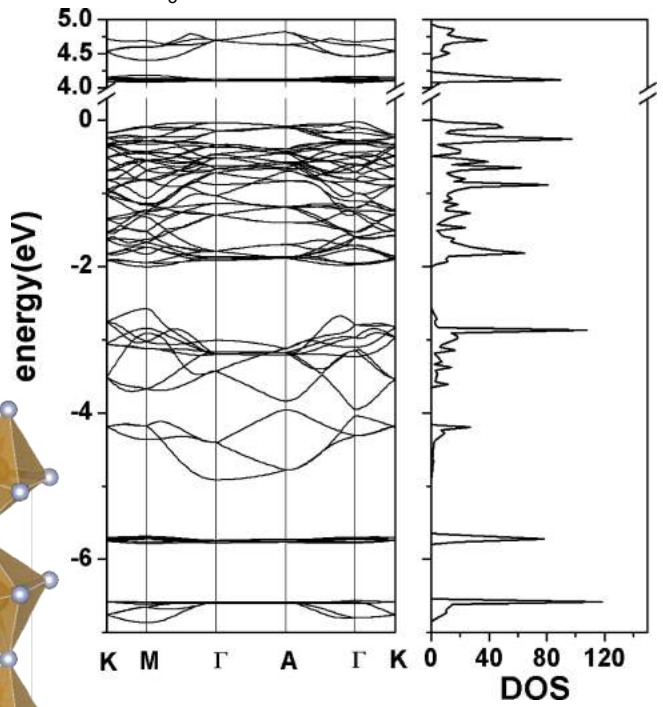
$$FeF_3 + 3Li^+ + 3e^- \longleftrightarrow Fe + 3LiF$$

This redox chemistry causes a problem for use as a cathode.

Rhombohedral FeF_3 Supercell



FeF_3 band structure from DFT (GGA + U)

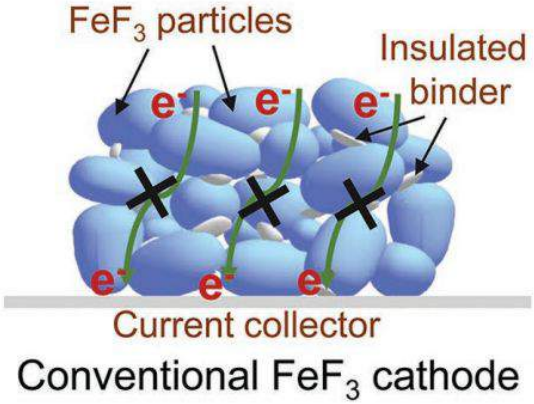


J. Phys. Chem. C 2010, 114, 39, 16813–16817

Carbon Enhanced Nanoconfinement

Degradation

- Carbon nanopores provide protection from metal dissolving into electrolyte



Conventional FeF_3 cathode

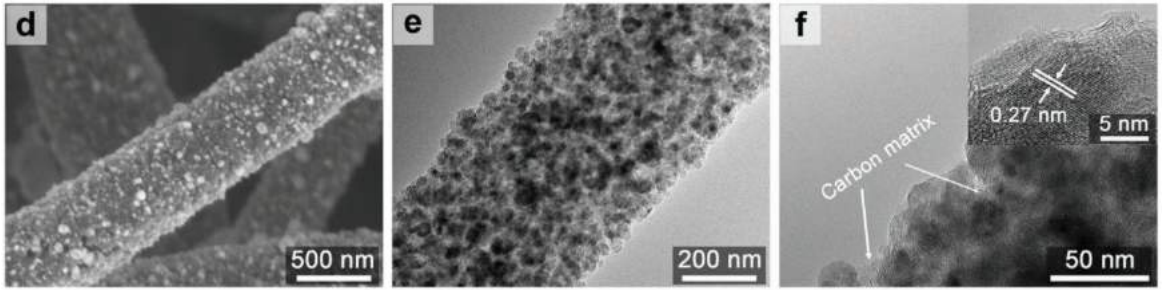
Fu, W., Zhao, E., Sun, Z., Ren, X., Magasinski, A., Yushin, G., *Adv. Funct. Mater.* 2018, 28, 1801711.

Confinement

- Active cathode materials confined
- Iron fluoride cannot escape carbon cage

Nanoconfinement

- Sufficiently small domains allow electrons to tunnel to reaction sites



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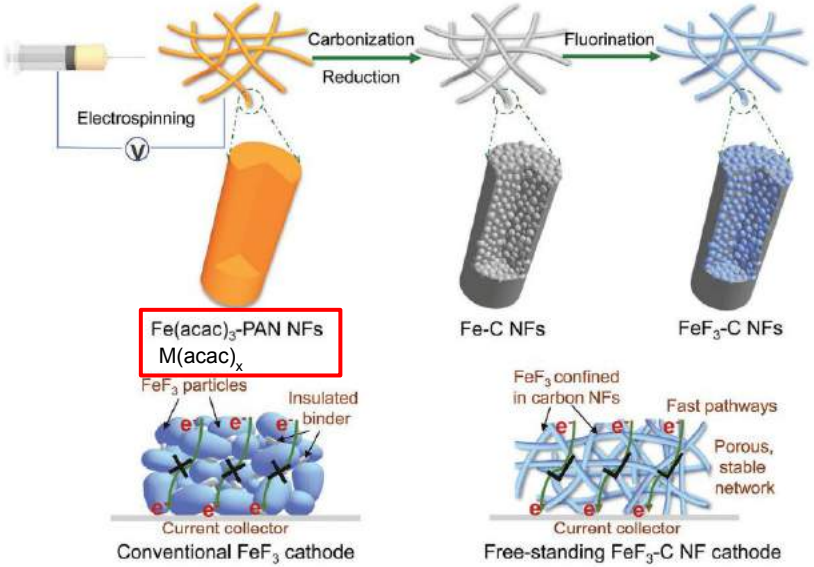
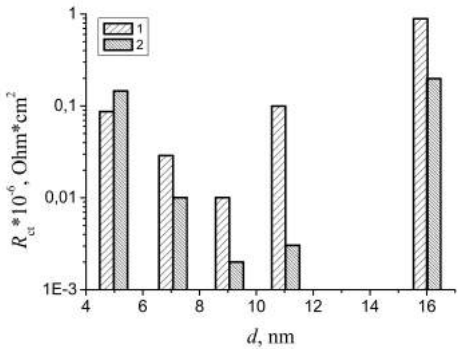
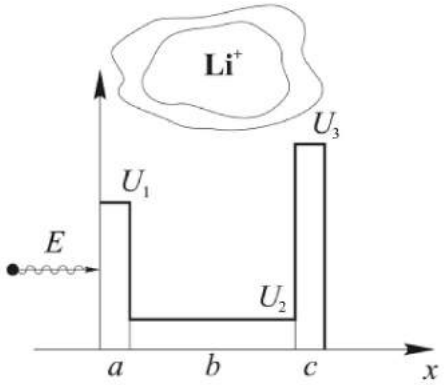
Carbon Enhanced Nanoconfinement on $FeMF_x$ Particles



Fu, W., Zhao, E., Sun, Z., Ren, X., Magasinski, A., Yushin, G., *Adv. Funct. Mater.* 2018, 28, 1801711.

- Mixed metal fluorides can be confined in carbon nanofibers (CNFs) by adapting CNF synthesis
- In addition to adding stability, nanoconfinement also has effects on electron transport





Lukiyanets, B. A., D. V. Matulka, and I. I. Grygorchak. *arXiv preprint arXiv:1106.5142* (2011).

Hypothesis:

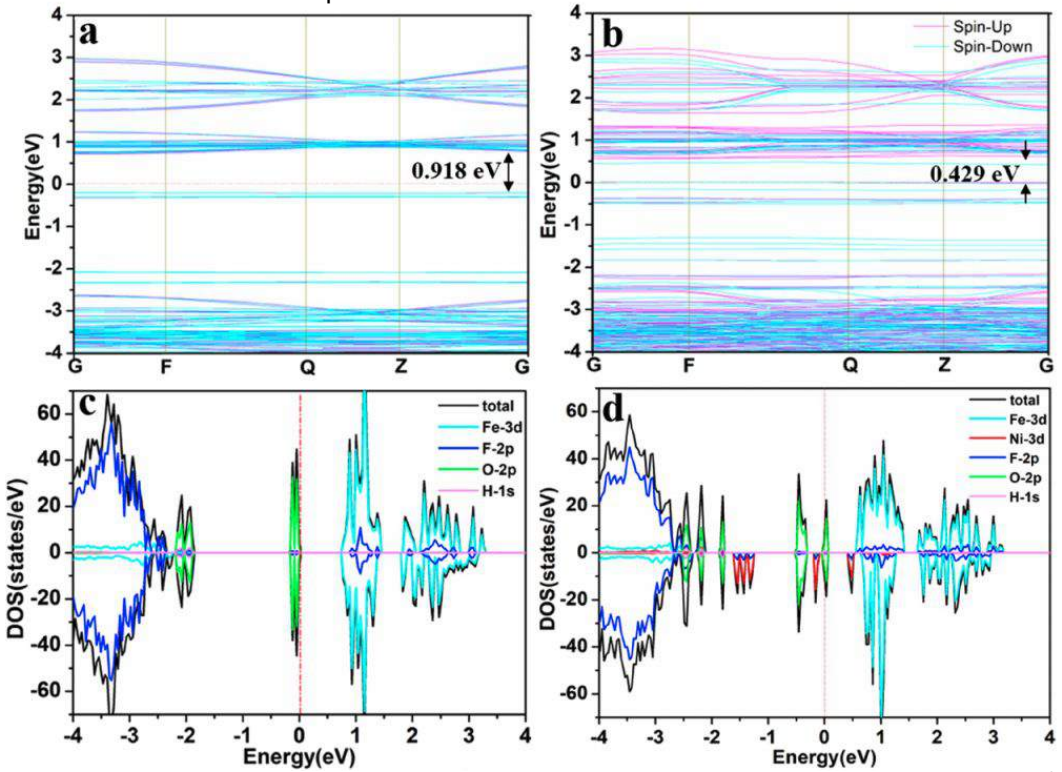
- Doping will reduce the bandgap and improve ion mobility

Doping Effects on Bandgap

- Working with FeF_3 water complexes, several groups have been able to introduce dopants that add an impurity band that falls in the bandgap

- The electronic band structure (above) and associated DOS (below) are shown for the undoped (left) and nickel doped (right) systems. Computed with GGA + U DFT

Computed band structure and DOS from DFT



ACS Sustainable Chem. Eng. 2020, 8, 15651−15660

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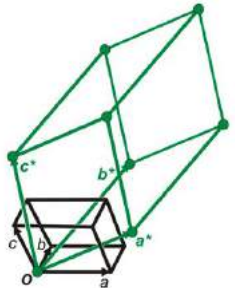
Experimental Framework

- DFT Calculations of possible mixed-metal fluoride nanoparticles to determine band structure.
  - Initial guesses of low-nickel doped FeF_3 structures
  - Appropriate exchange correlation, and K point density for good estimates of band structure
- Synthesis adapted from Fu et al.[1]
  - Mixed metal fluorides confined by electrospun CNFs
- XRD, SEM imaging
  - Investigate the structure of the nanoparticles and CNFs
- Electrochemical Impedance Spectroscopy (EIS) and capacity fading
  - Measure the impedance of constructed battery cell

Rhombohedral lattice & it's reciprocal

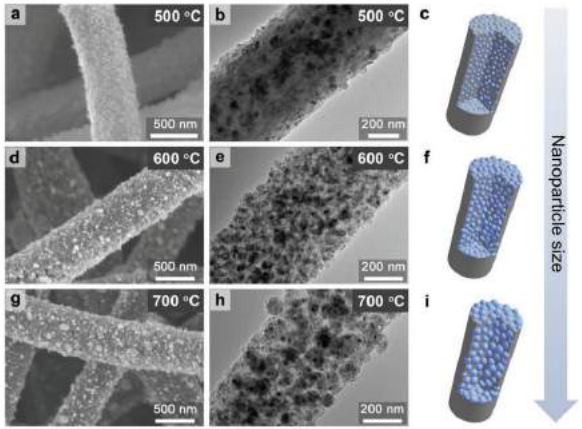


CSIC - Cristalografía y Biología Estructural

1. Fu, W., Zhao, E., Sun, Z., Ren, X., Magasinski, A., Yushin, G., *Adv. Funct. Mater.* 2018, 28, 1801711.

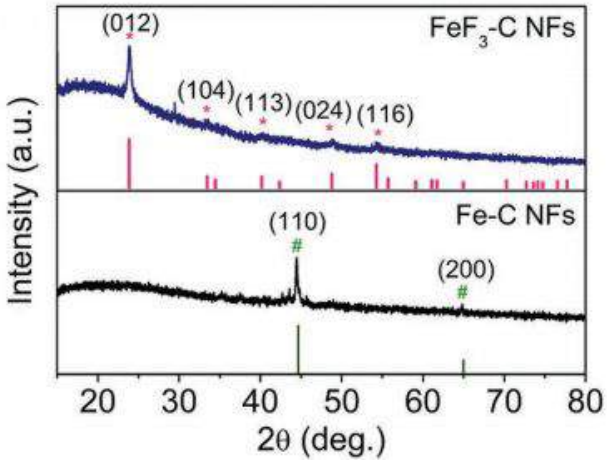
Experimental Validation

SEM/TEM: NP Size variation



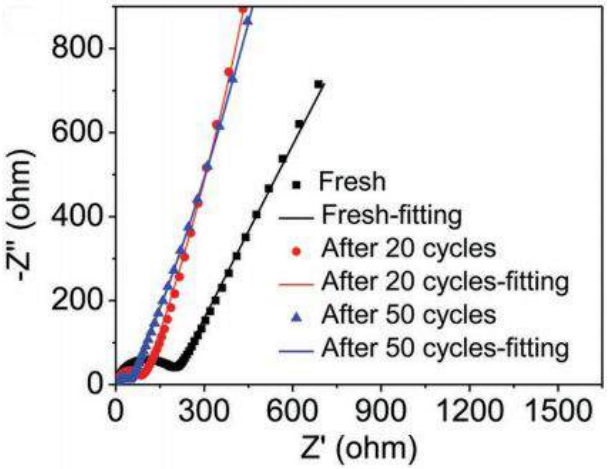
- Nanoparticle size optimization could enhance tunneling occurrence
  - Lowers impedance

XRD: FeF3 nanofibers formation



- We see the Fe-F bonds at 012 peak
- If our proposed synthesis is successful, we would expect to see a peak for M-F bonds

EIS: impedance of cell with cycling

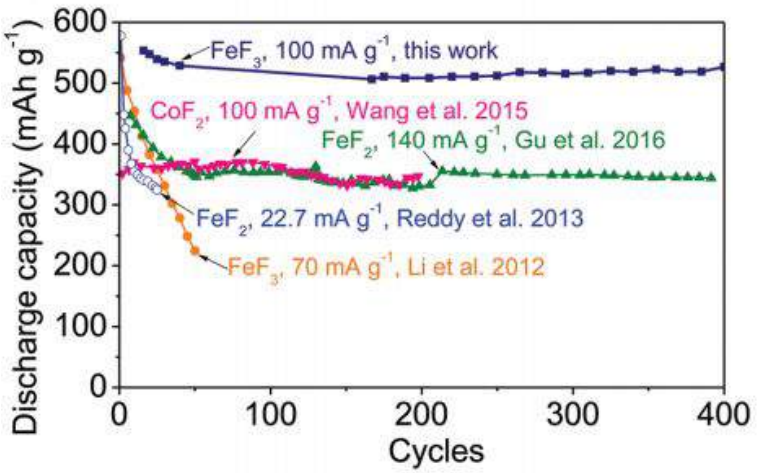


- Reduced charge transfer resistance (R_{ct}) from protection by the CNFs
- Doping should contribute to further lowered R_{ct}

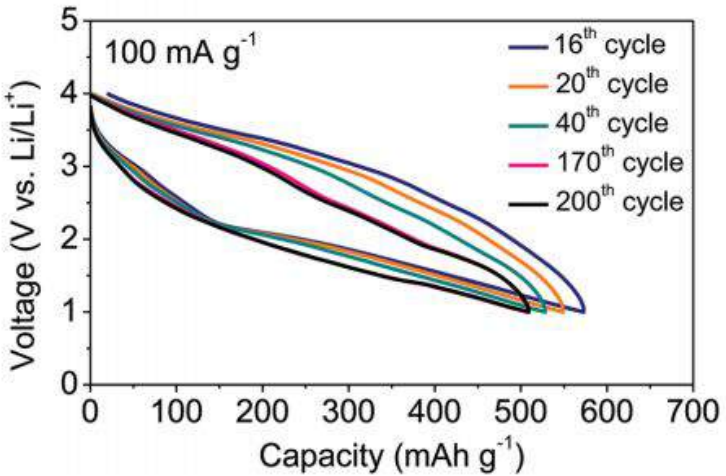
Fu, W., Zhao, E., Sun, Z., Ren, X., Magasinski, A., Yushin, G., *Adv. Funct. Mater.* 2018, 28, 1801711.

Images for Experiments

Capacity Stability



Voltage Profile



- CNFs FeF_3 more stable than other metal fluoride cathode configurations
- Reduced capacity and voltage loss after many cycles

Fu, W., Zhao, E., Sun, Z., Ren, X., Magasinski, A., Yushin, G., *Adv. Funct. Mater.* 2018, 28, 1801711.

Conclusion

- Impact of proposal
  - **Contribute to sustainable cathode materials research, primarily using Fe instead of Co**
  - **Use doping and nanoconfinement to enhance the desired properties of metal fluorides**

- We would like to acknowledge
  - Dr. Wangda Li, TexPower
  - Dr. Gleb Yushin, Sila Nanotechnologies

Thank You!

Are there any questions?