Pacific Northwest
NATIONAL LABORATORY

PNNL-32708

Low-temperature electroplating of zirconium: Ionic mixture methods

March 2022

Christina Arendt
Lance Hubbard

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical
Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL-32708

Low-temperature electroplating of zirconium: Ionic mixture methods

March 2022

Christina Arendt
Lance Hubbard

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

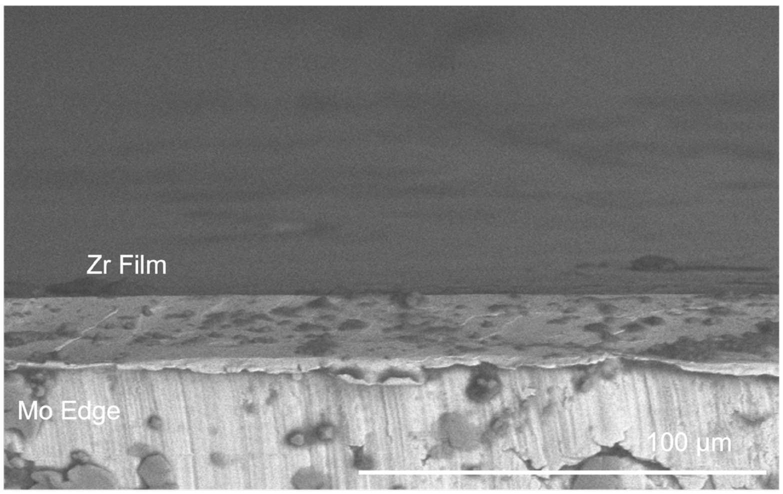
Pacific Northwest National Laboratory
Richland, Washington 99354

Acknowledgments

The research described in this report was conducted under the Laboratory Directed Research and Development (LDRD) Program as a strategic investment at the Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. PNNL is a multi-program national laboratory operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830.

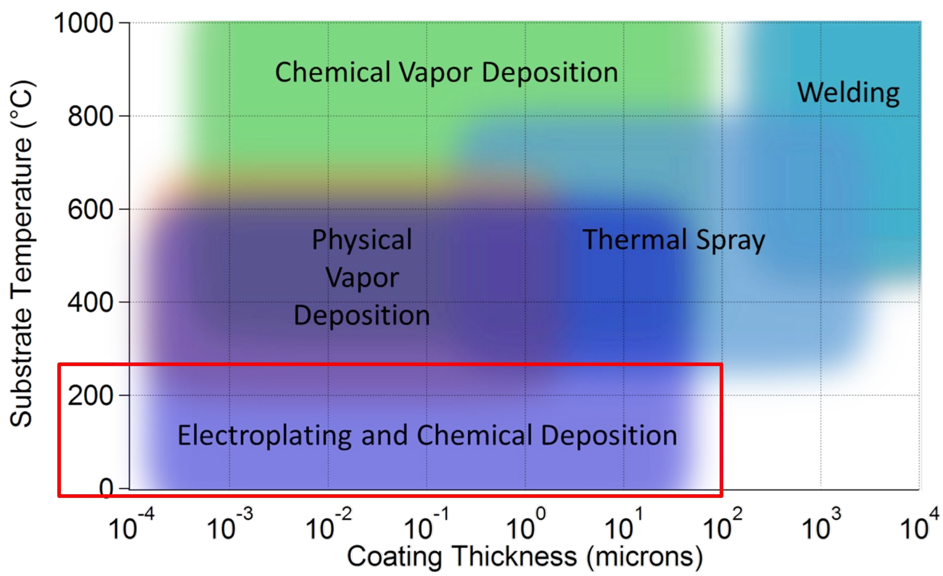
1.0 Results

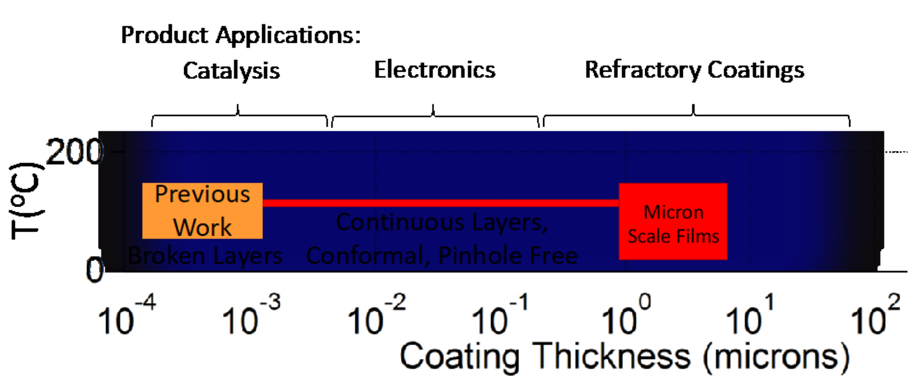
- Zr films up to 6 microns thick have been deposited on Mo substrates
- Contamination levels low
- Surface coverage is high
- Film quality higher & cost lower than other plating methods



2.0 Background & Motivation

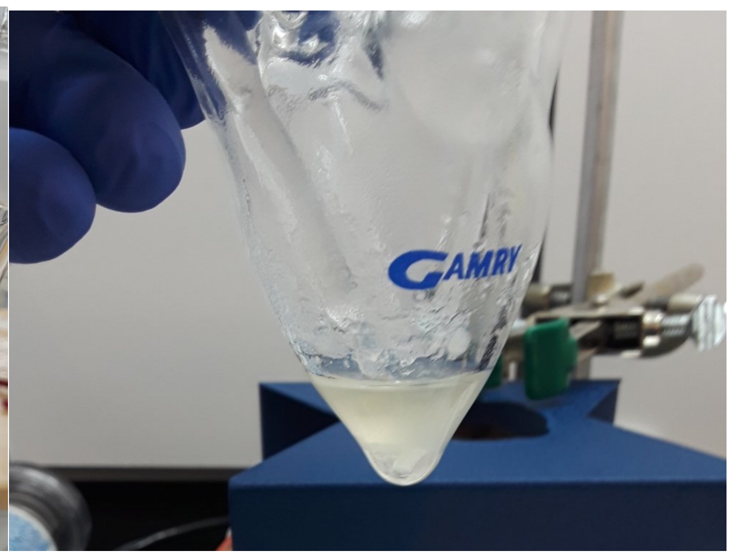
- Zirconium is a refractory metal
  - Useful for solar panels, electronics, furnaces, catalysis, etc.
  - Reduction potential past splitting point of water
- Current methods of plating Zr; all have issues
  - Co-rolling/co-extrusion
  - Applied coatings (plasma spray, sputter coating)
  - Molten salt electroplating
  - Ionic liquid (IL) electroplating
- Ionic mixtures
  - Deep eutectic solvents (DES)
  - DES/IL mixtures
  - Room temperature to 125 °C

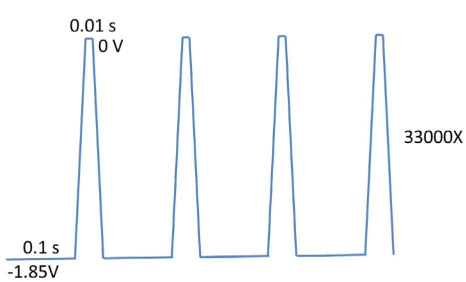




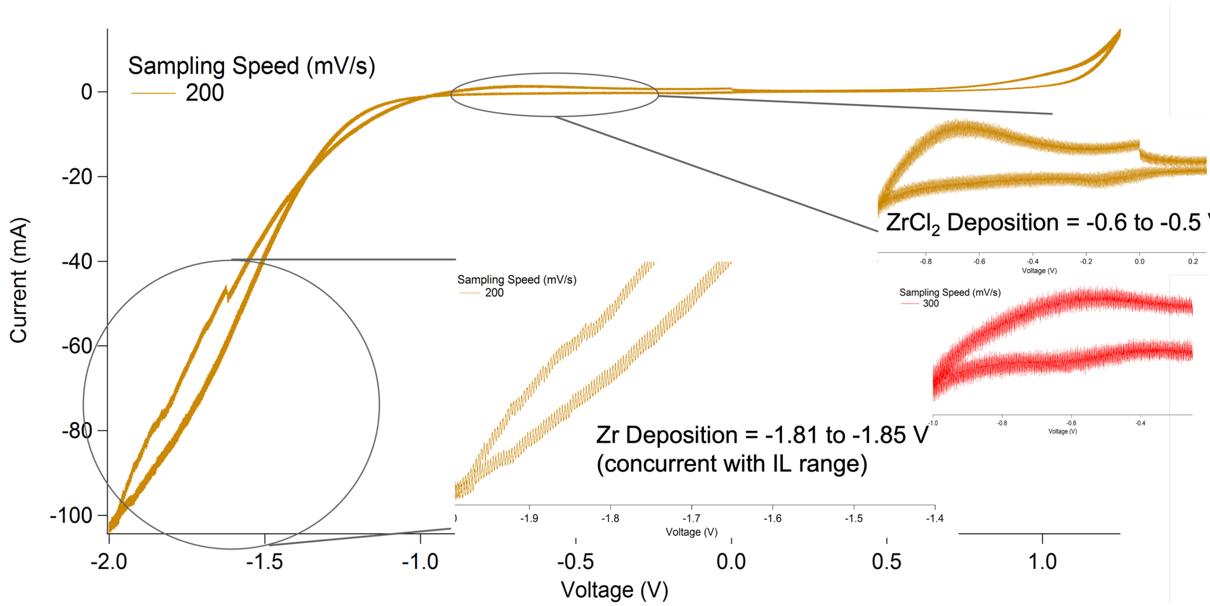
3.0 System Set-Up

- Gamry's Dr. Bob's Cell
  - Non-aqueous silver references
  - Glassy carbon electrode
  - ¼" wide Mo foils
- Deep Eutectic Solvent
  - Ethaline (1:2 choline chloride: ethylene glycol)
  - Ar cleaned under vacuum at 150 ^{o}C for 24 hours
  - +0.25 M ZrF_4 and LiF
- Electroplating
  - DC and AC both trialed
  - Pulse plating most successful
    - ✓ 100 ms plate, 10 ms rest
  - Stirred
  - Ar bubble and blanket
- Cyclic voltammetry study



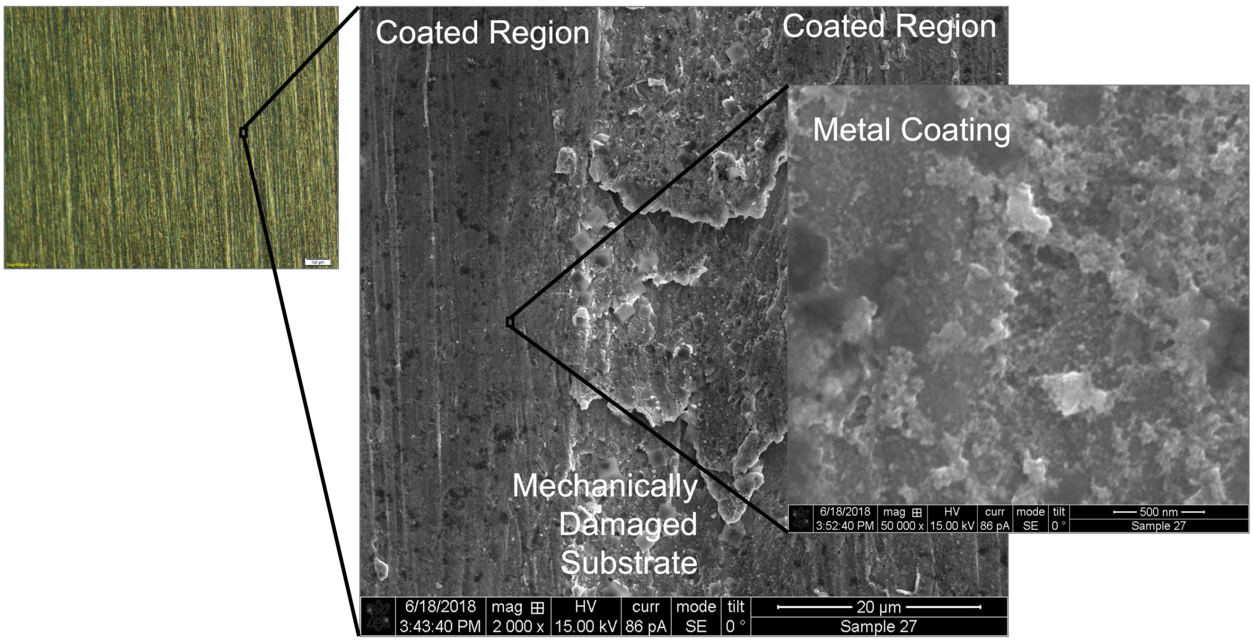


4.0 Cyclic Voltammetry

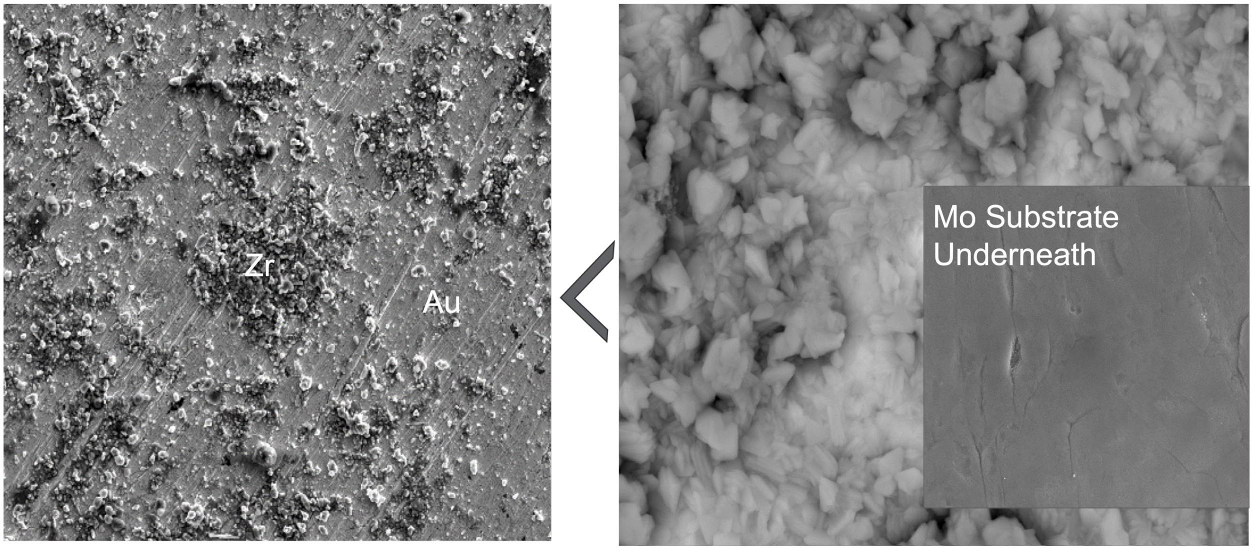


5.0 SEM Imaging, DC Plating

- Metal deposition
  - Coverage > 99.9±0.4%
- Isolated salts
- Porosity 0.01-0.1%
- Grains 30-50 nm

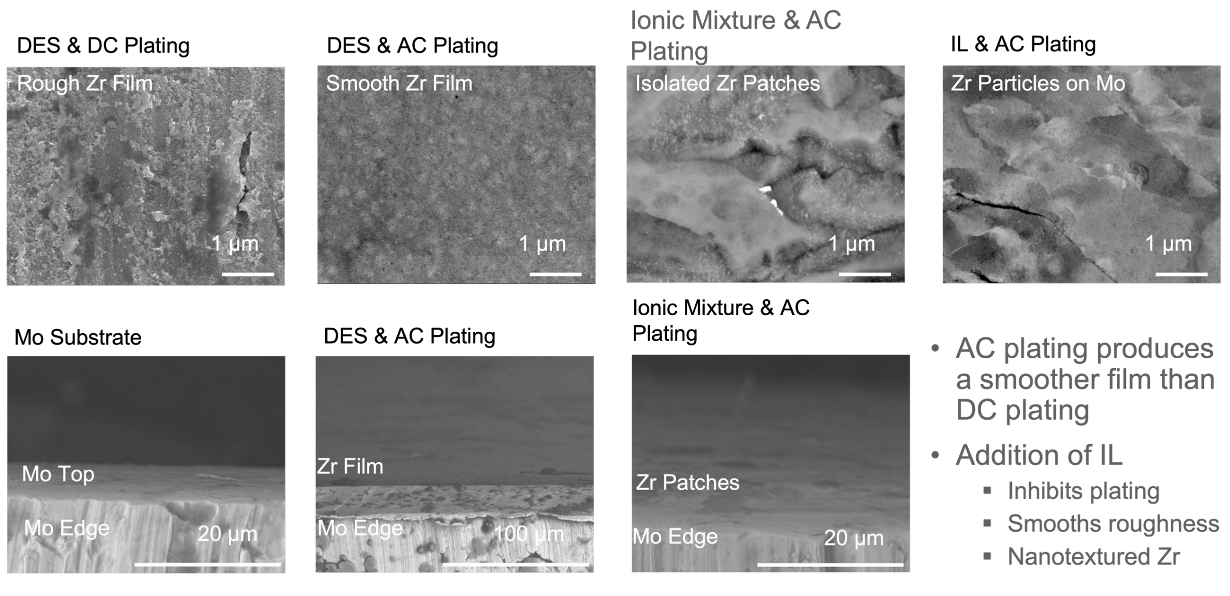


6.0 Literature vs. DC Plating Results

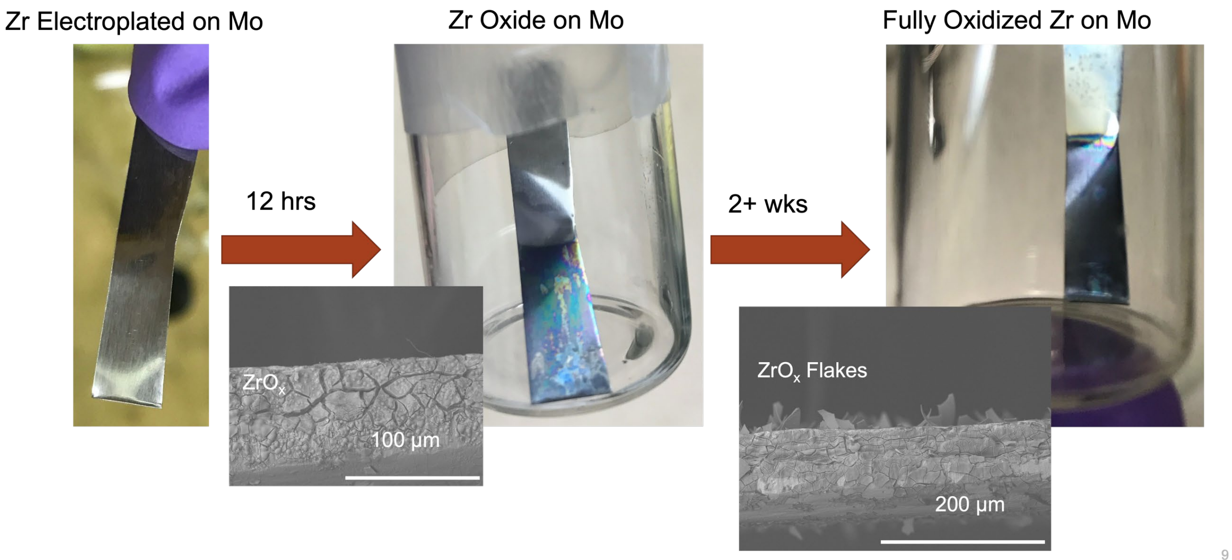


veprints.unica.it/1081/1/PhD_Thesis_LauraMais.pdf

7.0 Film Morphology

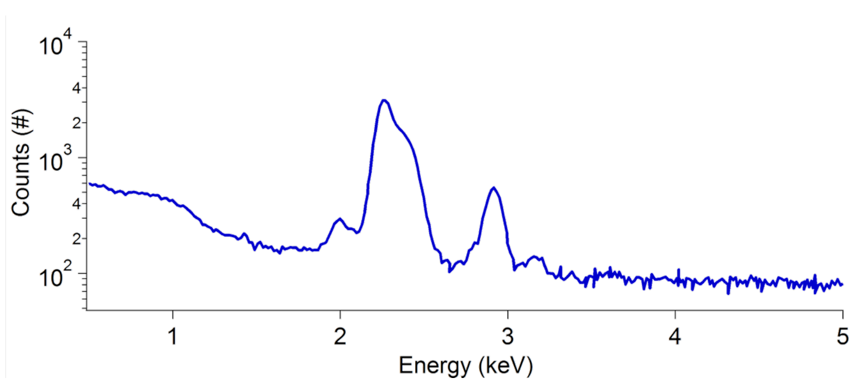


8.0 How do we know we have a metallic coating?

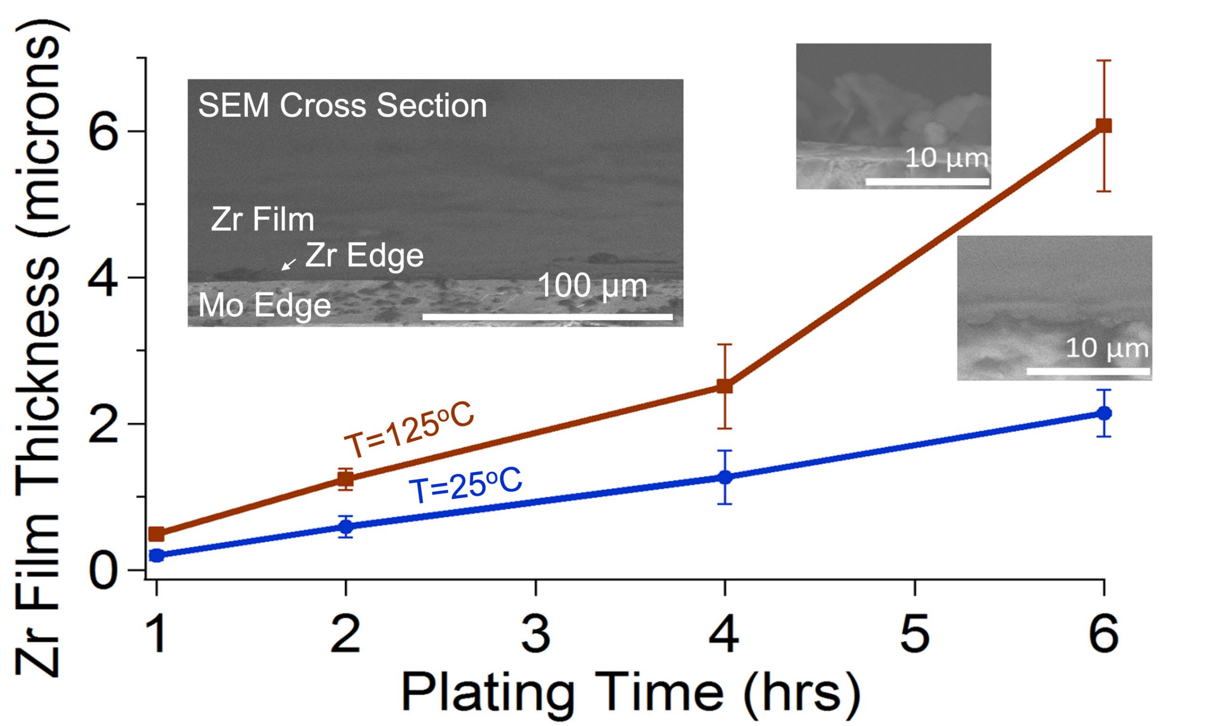


RF, XPS & XRD Help Confirm Metallic Zr

- XRF
  - Zr signal occludes Mo signal
    - ✓ Mo diminishes & Zr stable
  - S from 0.1 – 2%
  - Intermittent Cl from 0.1 – 0.3%
- XPS
  - ZrO (surface oxide) seen
- XRD
  - Metallic signature for Zr & Mo
  - No bulk oxides
  - No bulk sulfides
  - Some LiCl and ZrCl



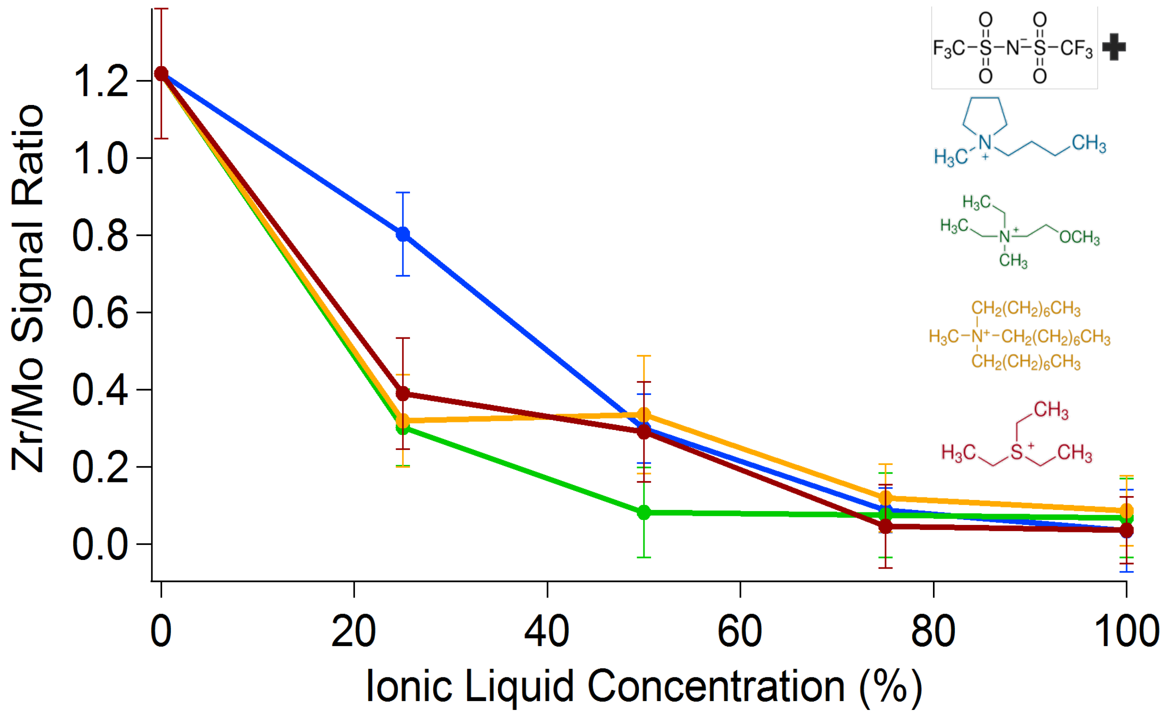
Time-Temperature Effects



Ionic Liquid Options

- Other cations
  - BMP short supply
  - Polarity & viscosity
  - BMP BTS (Best Prior)
  - DMA BTS (Polar, ↓µ)
  - MTA BTS (Non Polar, ↑µ)
  - TES BTS (Non Polar, ↓µ)
- Sulfur contamination
  - 2, 31, 12, 13%
  - S-Mo interference
- BMP BTS most reliable IL
  - Can be difficult to acquire
  - MTA BTS & TES BTS possible alternates
  - Smooth film deposition

How do we know we have a metallic coating?



Ionic Liquid Options

BMP BTS = 1-Butyl-3-Methyl-Pyrrolidium Bis (Trifluoromethylsulfonyl)imide

DMA BTS = Diethylmethyl (2-Methoxyethyl)Ammonium Bis (Trifluoromethylsulfonyl)imide

MTA BTS = Methyl-Trioctylammonium Bis (Trifluoromethylsulfonyl)imide

TES BTS = Triethylsulfonium Bis (Trifluoromethylsulfonyl)imide

9.0 Conclusion

- Demonstrated conformal Zr platings at low temperatures
- Deposition of metallic Zr Film from DES
  - DC plating: 100s of nm thick
  - AC plating: 6 microns, smoother, cleaner
- ILs can be used as a growth inhibitor
- ZrF_4 is more soluble in DES than IL
  - Greatly improves deposition
- Deposition is diffusion limited
  - Pulse plating improves deposition
- Moving on to other metals of interest

Pacific Northwest National Laboratory

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99354

1-888-375-PNNL (7665)

www.pnnl.gov