Molten Salts in Extreme Environments Energy Frontier Research Center Overview and Update

James Wishart, MSEE Director, *Brookhaven National Laboratory*

MSEE assembles unique expertise and capabilities across nine institutions to accomplish multimodal, multidisciplinary research that would be impossible at a single institution

MSEE molten salts in extreme environments

9 Institutions, 19 Principal Investigators, 24 Postdocs, students and staff

Molten salt synthesis (lab-scale)

X-ray and neutron studies of salt and solute structure in the bulk and at interfaces

Classical, *ab initio* and NN molecular dynamics simulations

Radiation chemistry

X-ray, optical and Raman Spectroscopy

Actinide chemistry

Electrochemical corrosion studies

Electron microscopy corrosion studies

X-ray tomographic imaging and multimodal synchrotron characterization

Phase-field modeling (transport of materials and phase boundaries)

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MSEE Research Strategy

We seek **molecular-level insight** into the workings of molten salts and their interactions with solutes, radiation and materials, by:

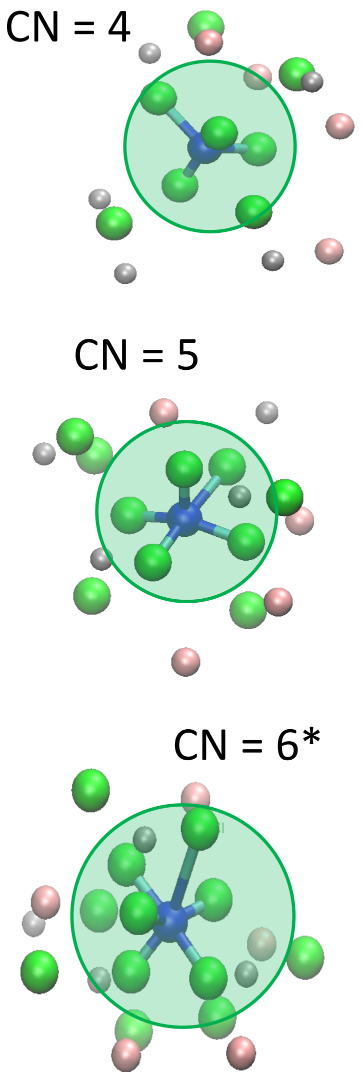
- **Developing and using molten salt experimental tools** to take advantage of the **advanced measurement capabilities of today's synchrotrons, neutron sources, and particle accelerators**,
- In combination with **state-of-the-art calculations** that can give us the means to **interpret our observations on such complex systems and predict molten salt behavior.**

We study *fundamental* problems (structure, speciation, corrosion), but...

We are well connected with the larger molten salt community doing applied science

Co-organizing yearly Molten Salt Chemistry symposia at Fall ACS Meetings since 2019

See you in Chicago, August 23-27, 2026! – 4 sessions and 38 presentations



Ab-initio MD: coordination states of Ni^{2+} in $KCl\text{-}MgCl_2$

Questions about the radiolysis of molten salts

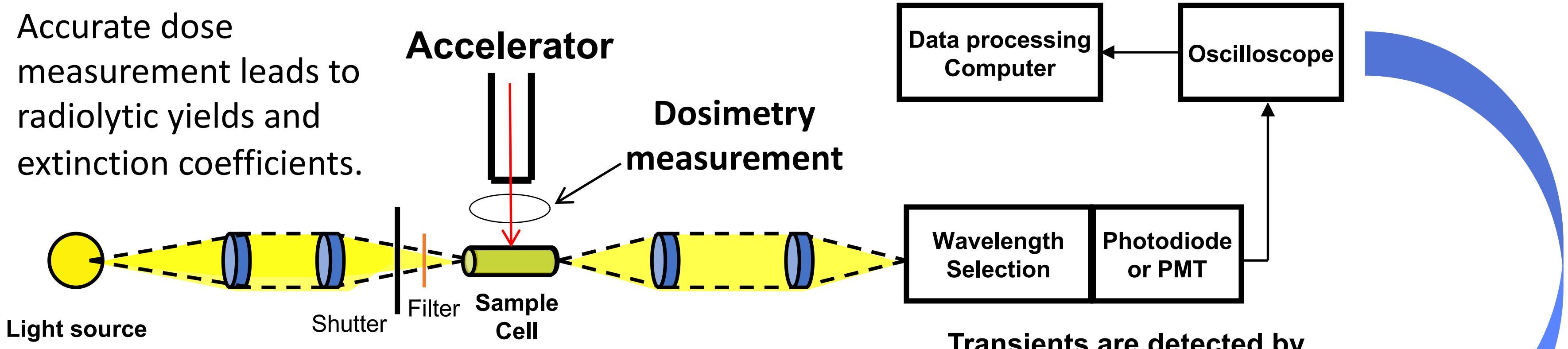
- What are the yields, speciation, and radical chemistries of the primary molten salt radiolysis products?
- How does radiolysis drive the redox speciation of solutes in molten salt fuel through its working lifetime?
- How does the irradiation of metal-ion laden molten salts lead to the formation of long-lived species (e.g., polyhalides, metal nanoparticles)?

Detection of radiation-induced transient species & reactivity in molten salts by pulse radiolysis

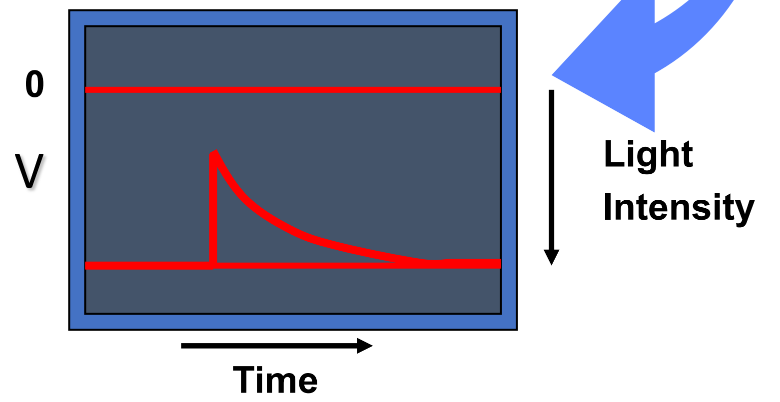
MSEE molten salts in extreme environments

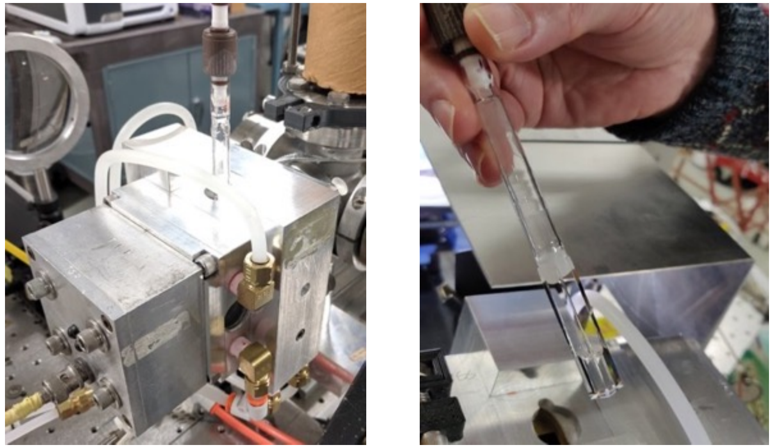
Fast reaction kinetics and radiolytic yields can be observed as functions of time to elucidate reaction mechanisms.

Accurate dose measurement leads to radiolytic yields and extinction coefficients.



Transients are detected by optical absorption changes.





High-temperature sample holder
Rev. Sci. Instrum. **91**, 083105 (2020)

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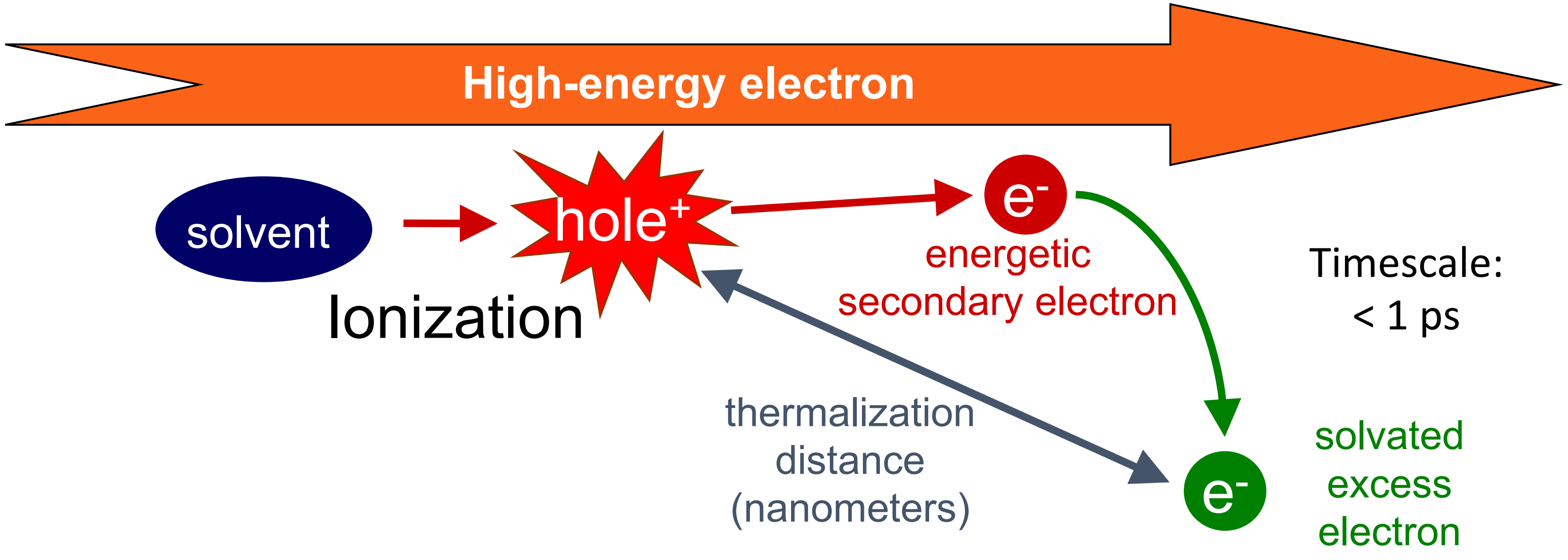
Initial events in radiolysis

High-energy electrons transfer energy to the medium, resulting in ionization of the constituents.

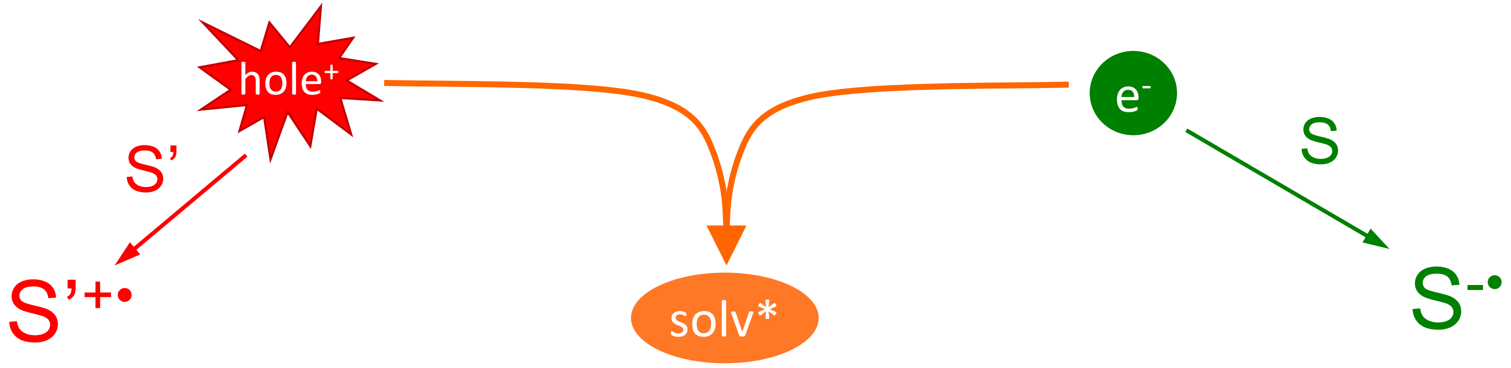


Timescale:
< 1 ps

The “hole” is where the electron used to be.
It is also a very reactive chemical species.

Primary radiolytic species reactivity in molten salts

Processes that control product distributions and fixation of radiation damage:



Electron-hole recombination

Solvated electron capture

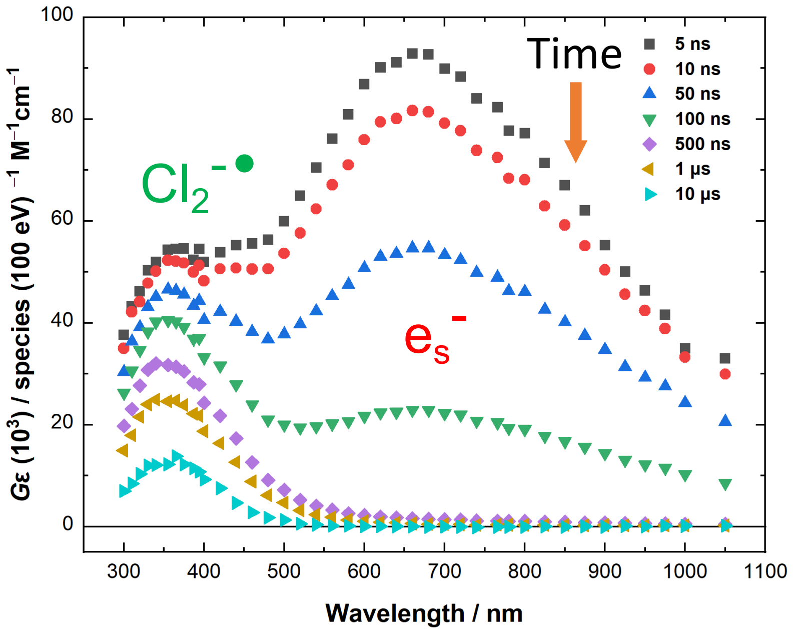
Solvated hole capture

Recombination of **S'+•** and **S-•**

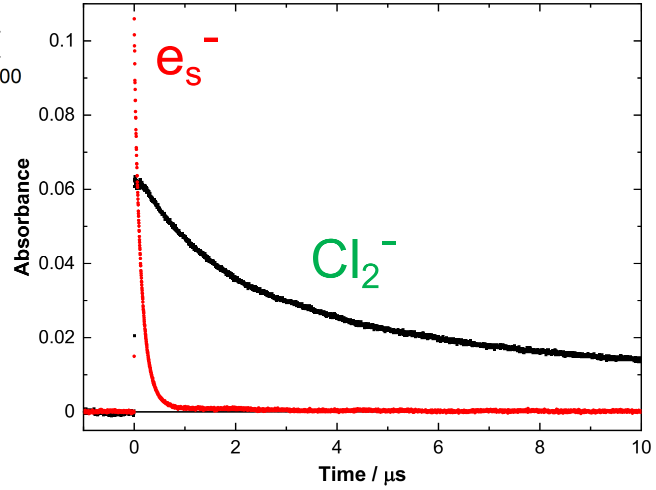
Conversion of **S'+•** and **S-** into permanent products

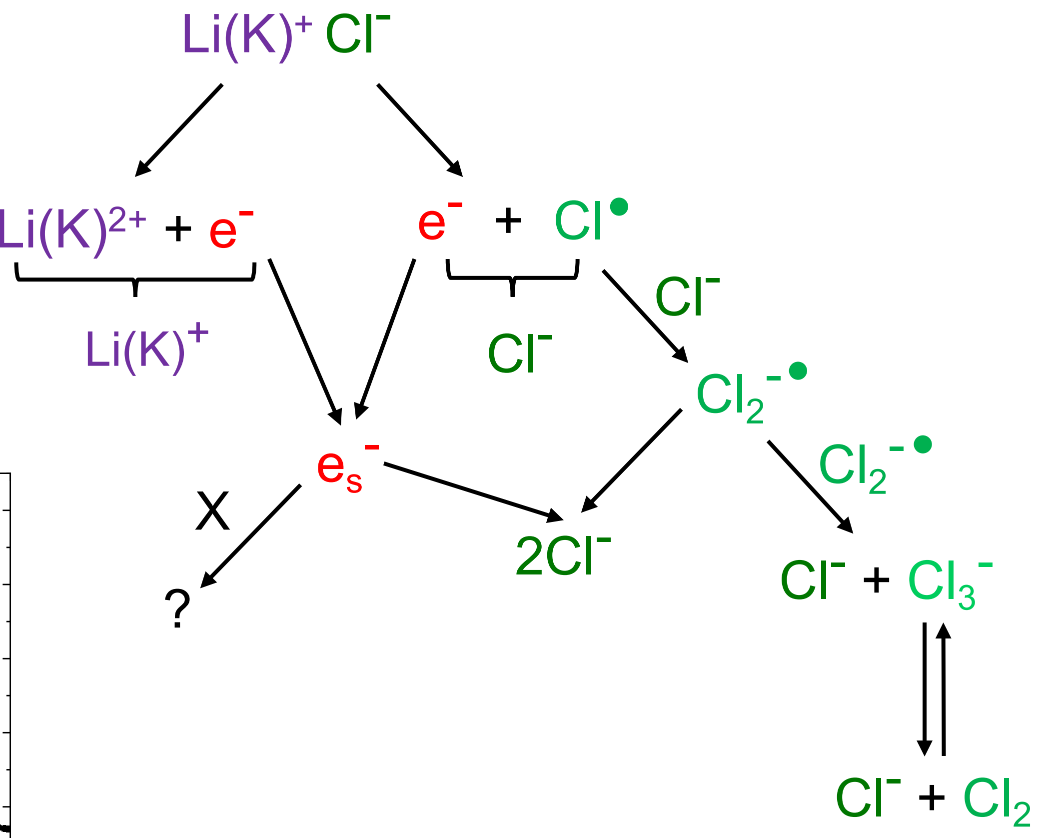
Radiation-driven chemistry of molten salts

Chloride salt radiolysis scheme in eutectic LiCl-KCl (42:58)



Spectra and kinetics at 400 °C
Melting point: 352 °C

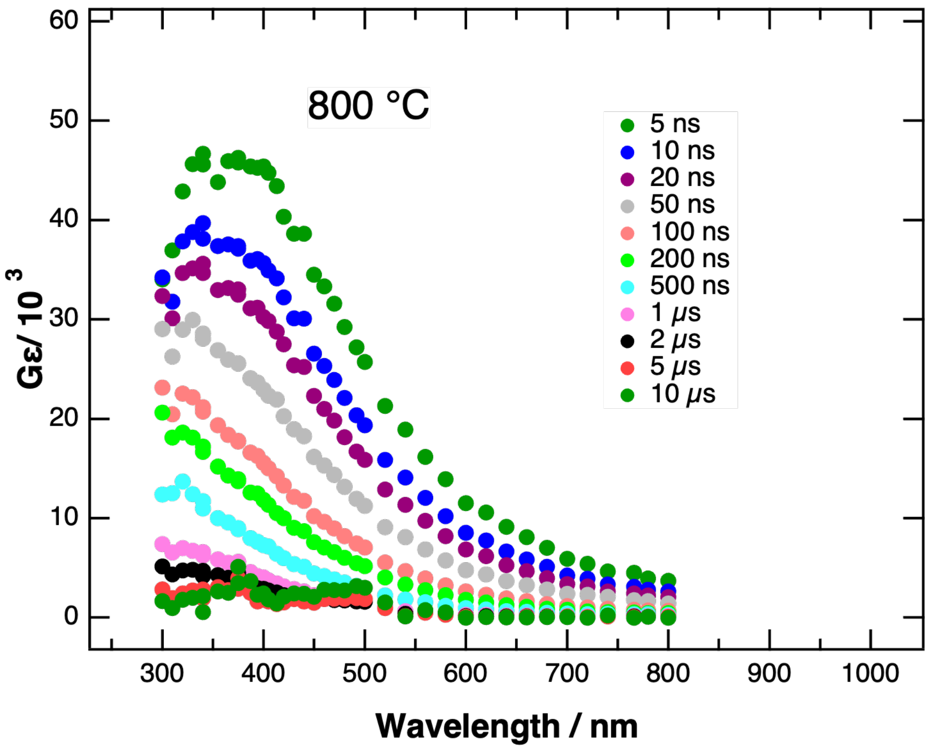




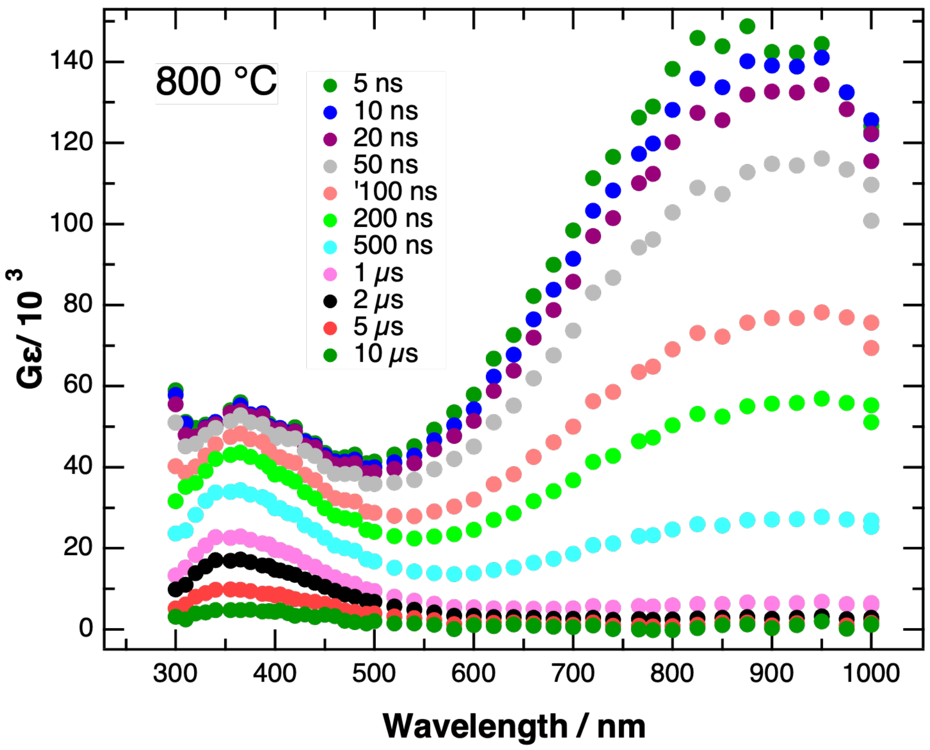
Speciation and reactivity of the solvated electron in the binary $MgCl_2$-KCl system

Excess electron spectrum in pure $MgCl_2$ is strongly blue-shifted compared to KCl and LiCl-KCl

100 % $MgCl_2$

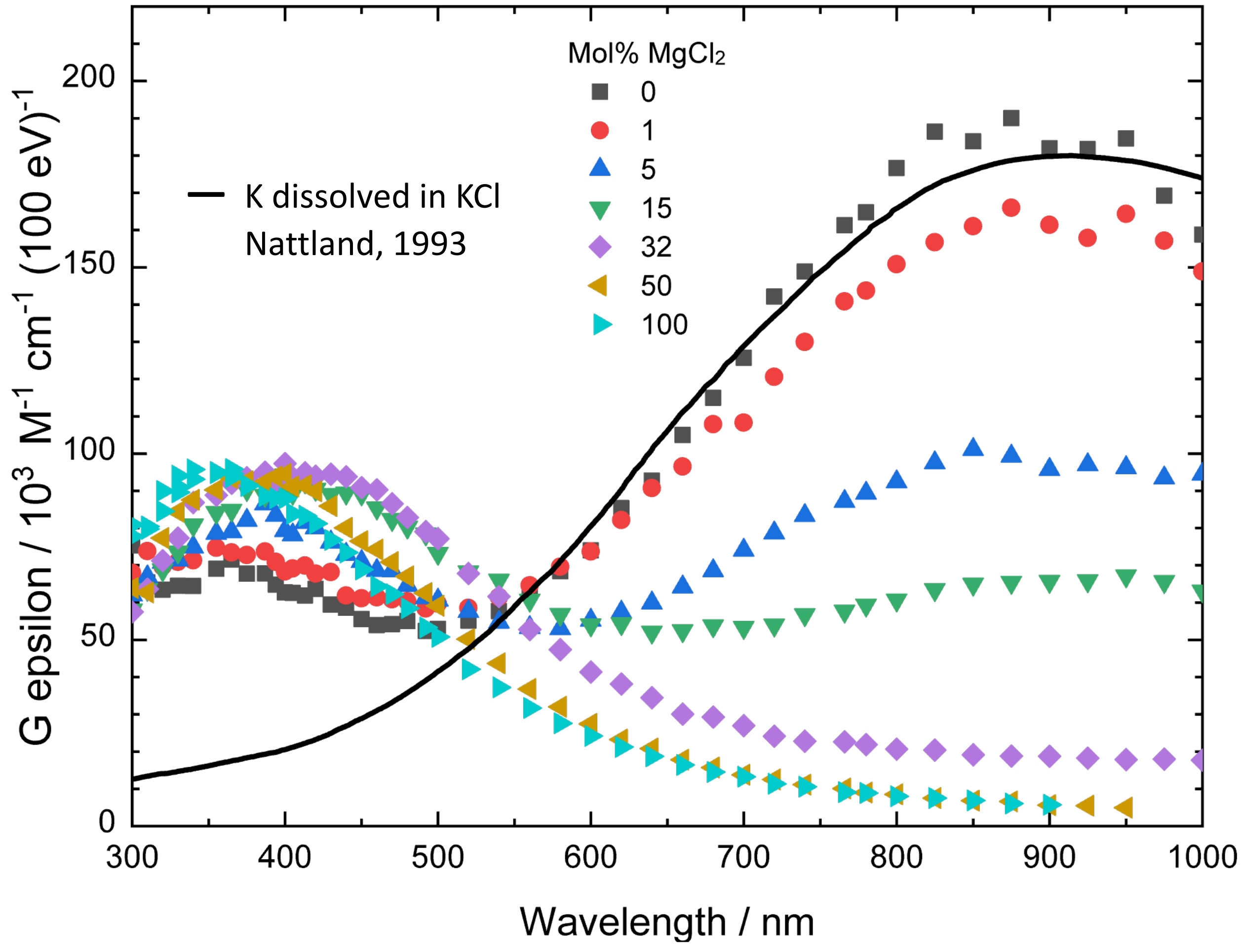


100 % KCl

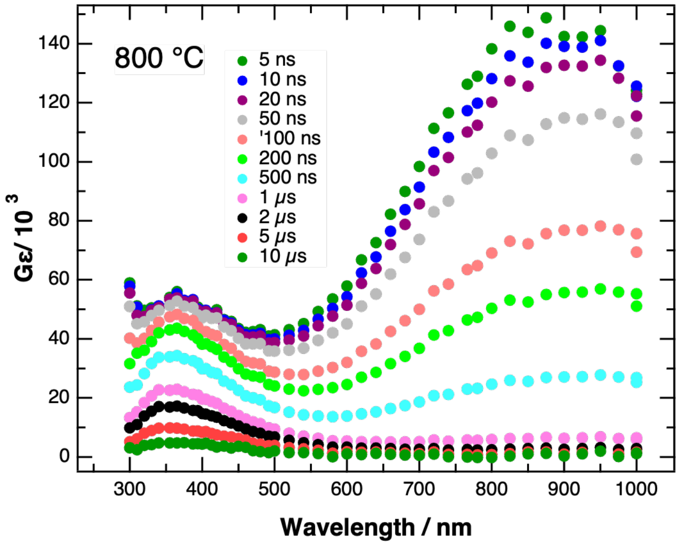


Spectroscopic investigation of the intermediate mixtures can reveal the electron solvation environments.

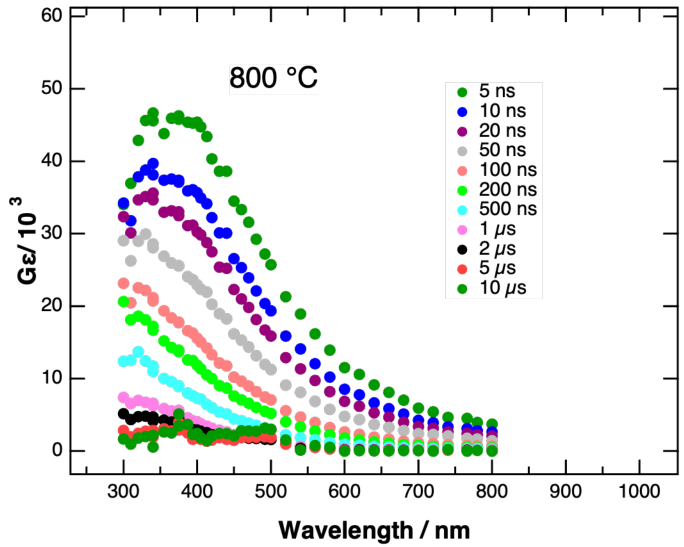
As Mg^{2+} concentration increases, the amplitudes of absorption bands change, but their positions do not; 3 species are implicated



Experimental radiolysis spectra by Kaz Iwamatsu.



100 % KCl

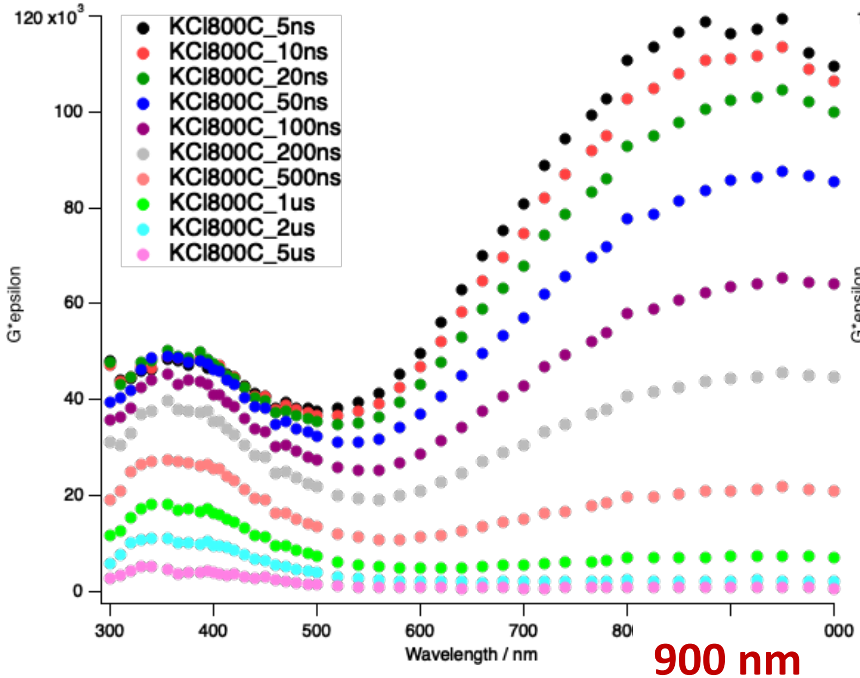


100 % $MgCl_2$

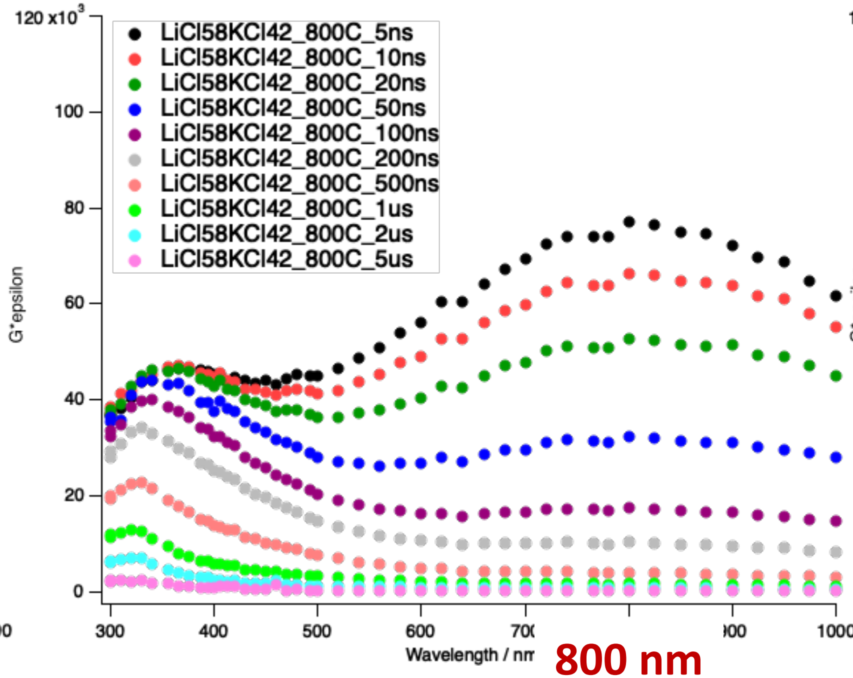
In contrast, solvated electron spectra shift smoothly with composition in the LiCl-KCl system

Measured at 800 °C

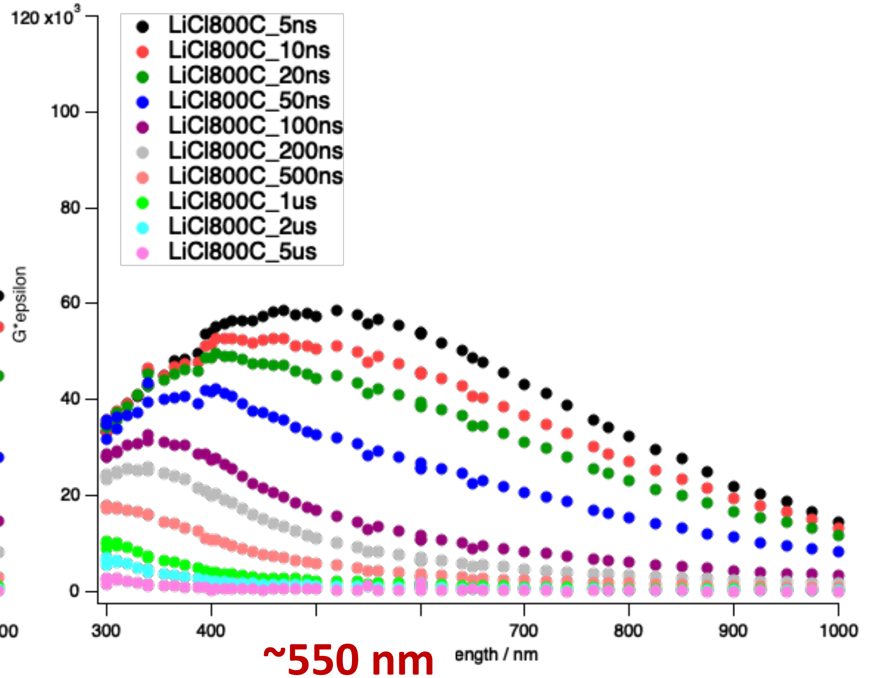
100% KCl



Eutectic: 58% KCl, 42% LiCl



100% LiCl

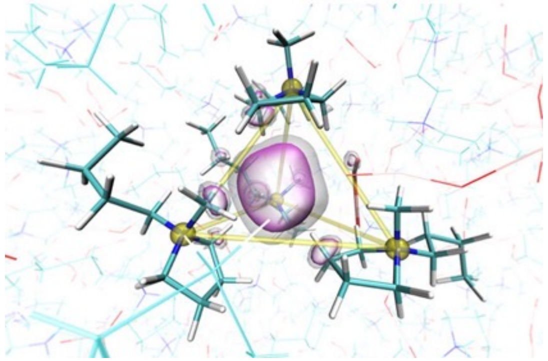


More polarizing Li^+ ion moves the electron spectrum to the blue compared to pure KCl.

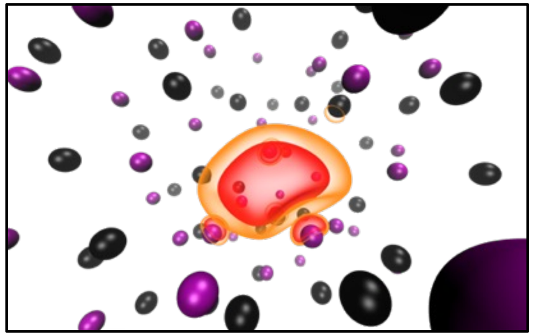
Solvated electron spectra in solvents of different polarity – the “cavity” model

Cavity e⁻

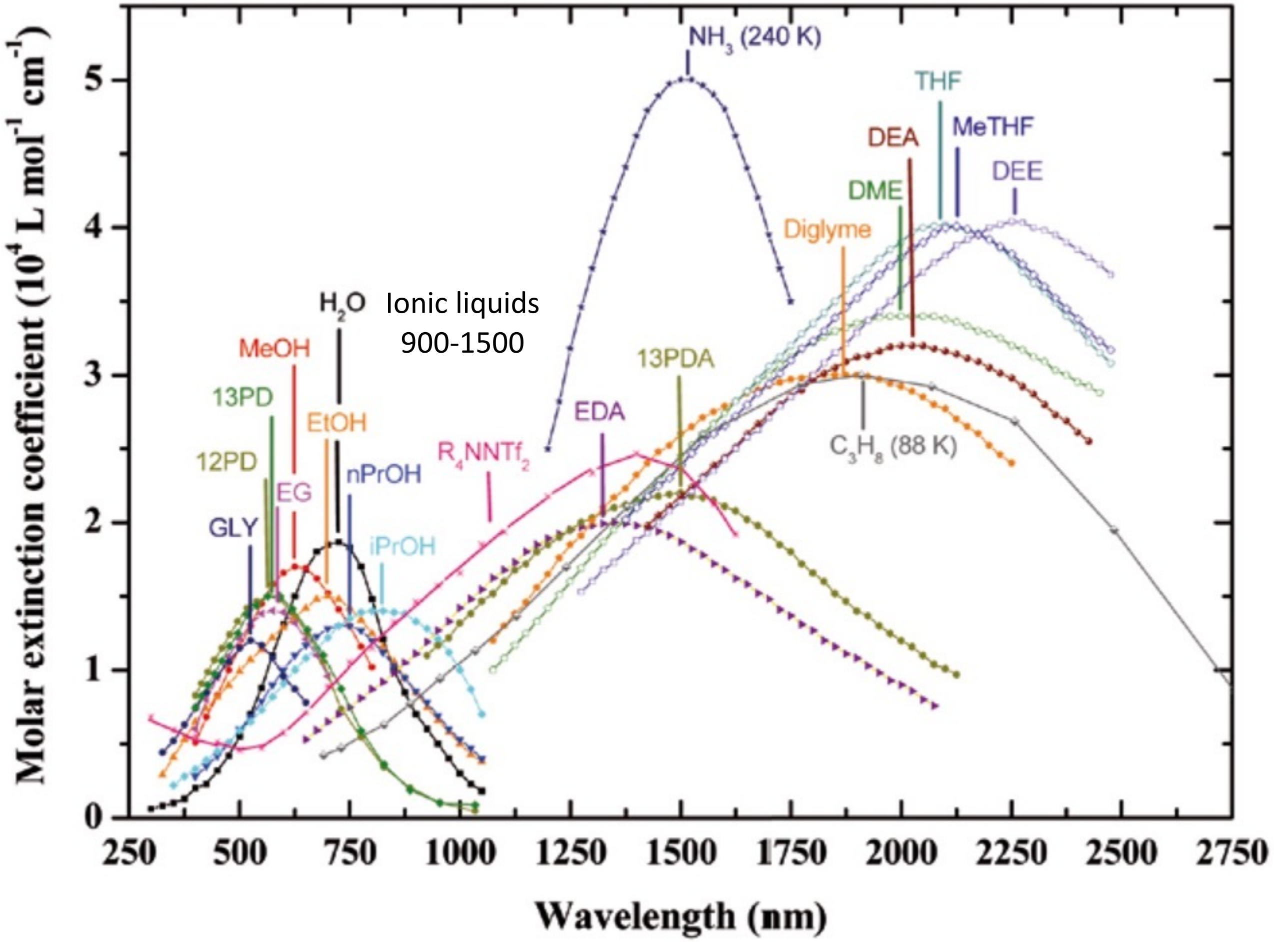
Ionic liquid



molten salt

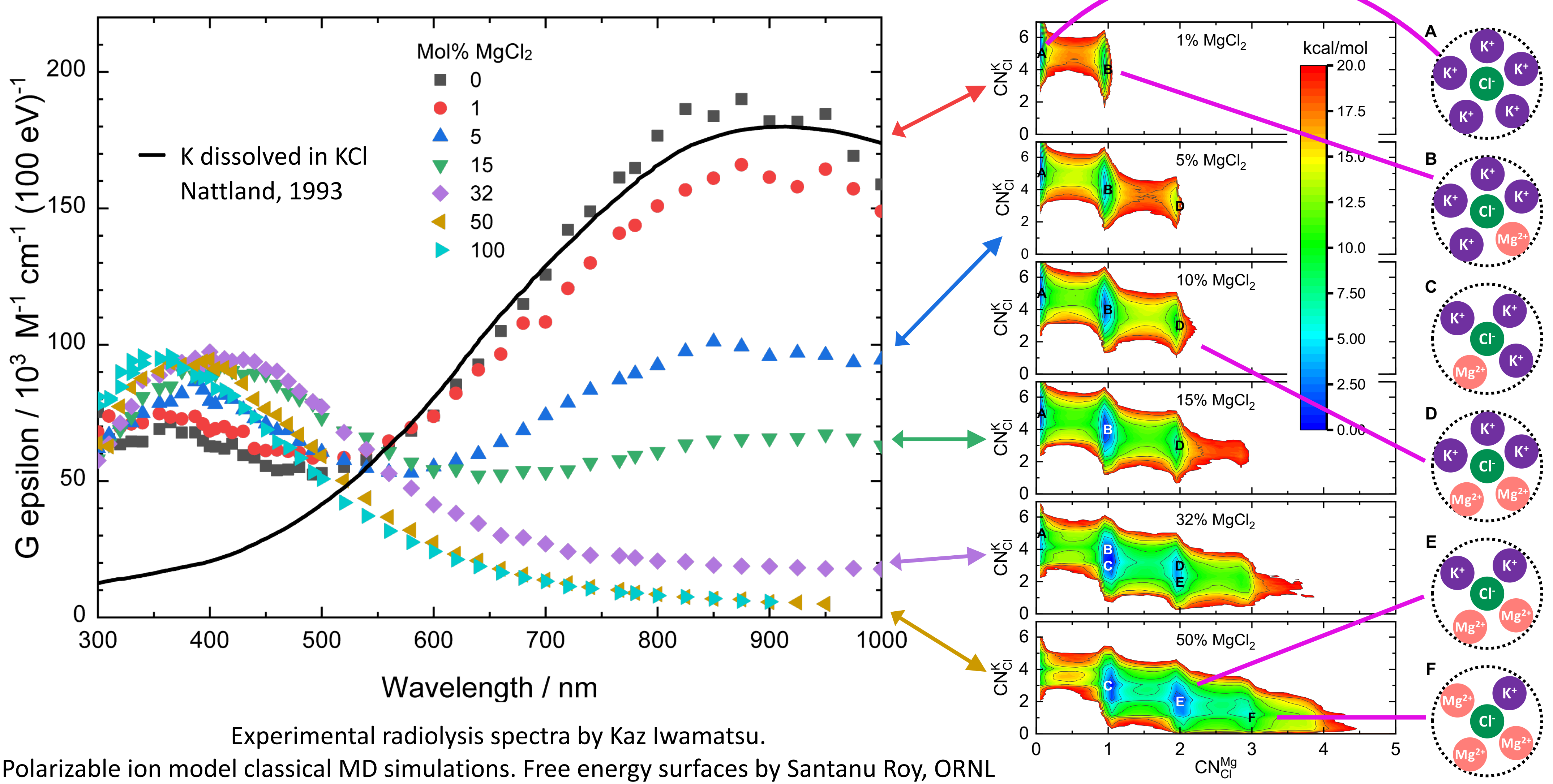


Alcohols and water
Polar solvents
Ethers and hydrocarbons



Mostafavi, M.; Lampre, I., in *Radiation Chemistry: From Basics to Applications in Material and Life Sciences*, Belloni, J.; Douki, T.; Mostafavi, M.; Spotheim-Maurizot, M., Eds. EDP Sciences: Paris, 2008; p. 40. (After Dorfman.)

A cavity-type model based on the simulated Cl^- coordination environment in $MgCl_2$-KCl salt mixtures can account for 3 species



Experimental radiolysis spectra by Kaz Iwamatsu.

Polarizable ion model classical MD simulations. Free energy surfaces by Santanu Roy, ORNL

Molecular Dynamics Shows Emergent Intermediate-Range Structure in $MgCl_2$-KCl

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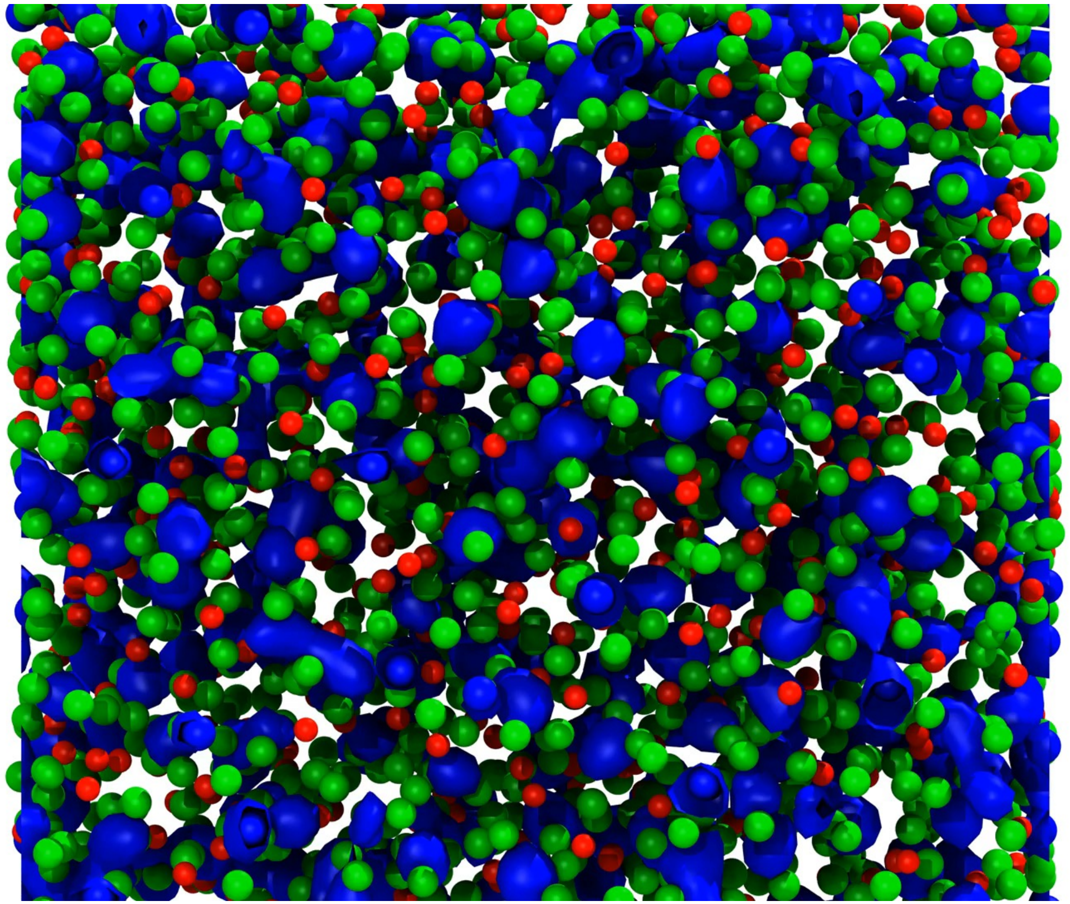
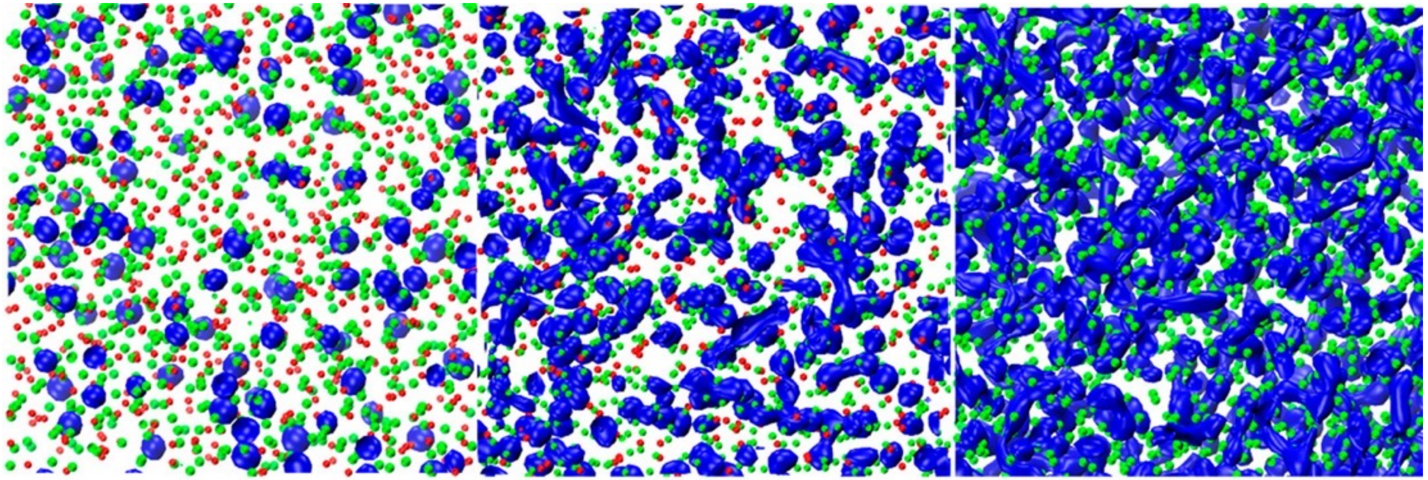
$KMgCl_3$

Multivalent (2+, 3+, 4+) ions induce clustering and networks.
Monovalent (1+) ions are the spacers between the networks.



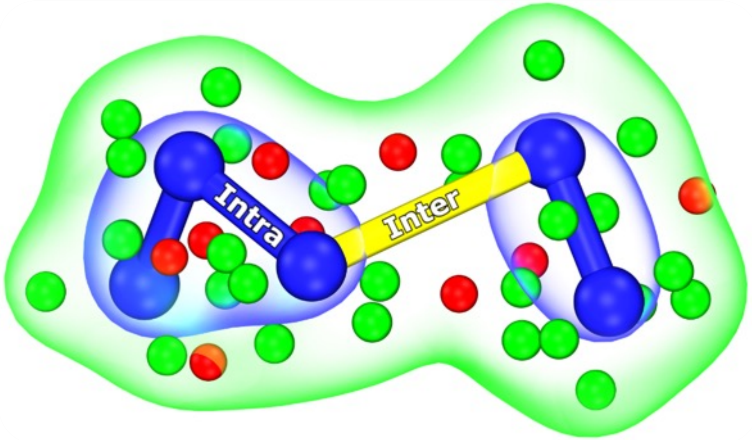
Networked liquids

15% $MgCl_2$ 50% $MgCl_2$ 100% $MgCl_2$



Blue **Mg^{2+}**
Red **K^{+}**
Green **Cl^{-}**

Blue isosurfaces highlight short transient **Mg^{2+} network**



Wu, F., *et al. J. Phys. Chem. Lett.* **2019,** *10*, 7603; *J. Phys. Chem. B* **2020,** *124*, 2892

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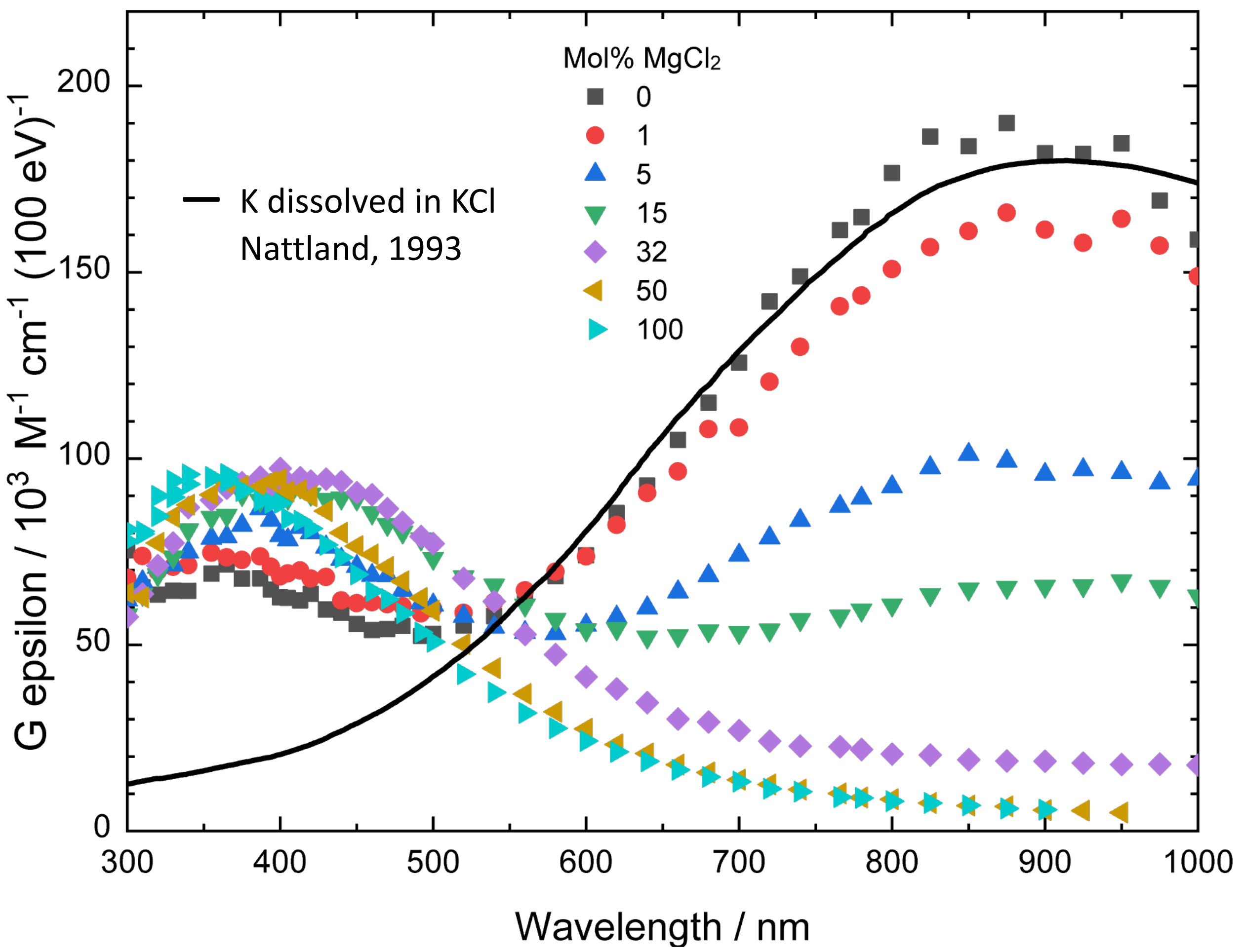
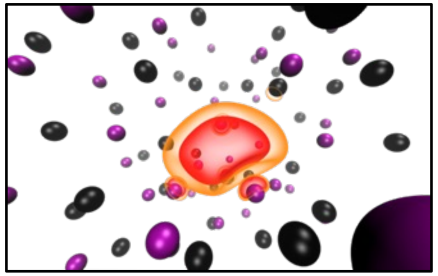
AIMD attributes the 3 species to a cavity electron at low [Mg2+], and two Mg-bound species at higher [Mg2+]

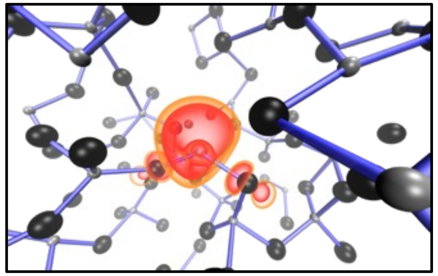


Experimental radiolysis spectra by Kaz Iwamatsu.
AIMD simulations by Hung Nguyen

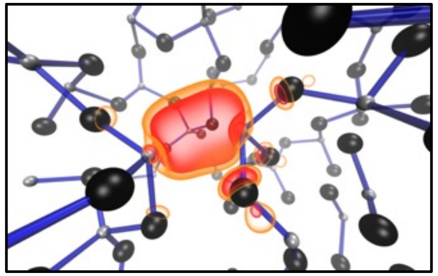
cavity e⁻



monomer

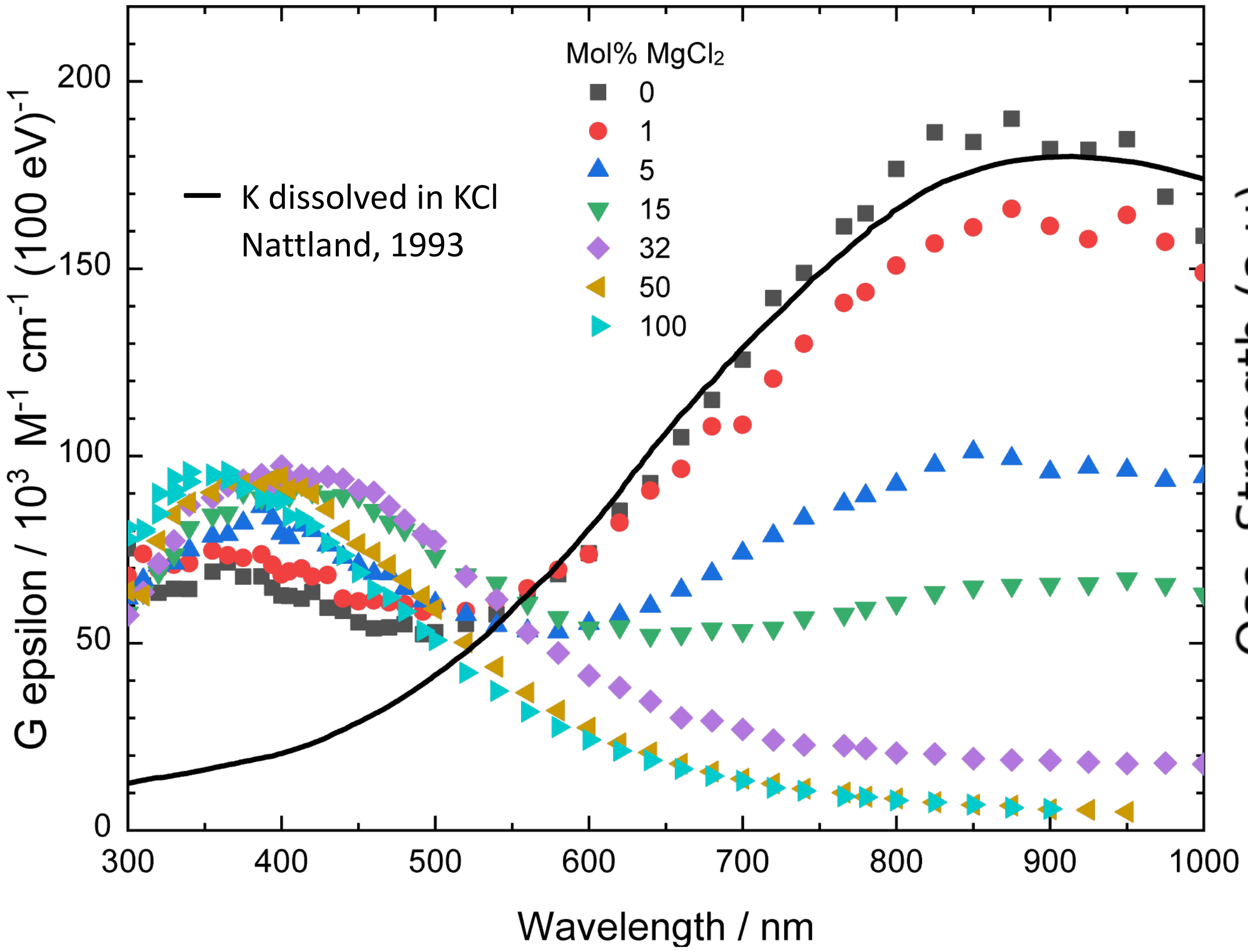


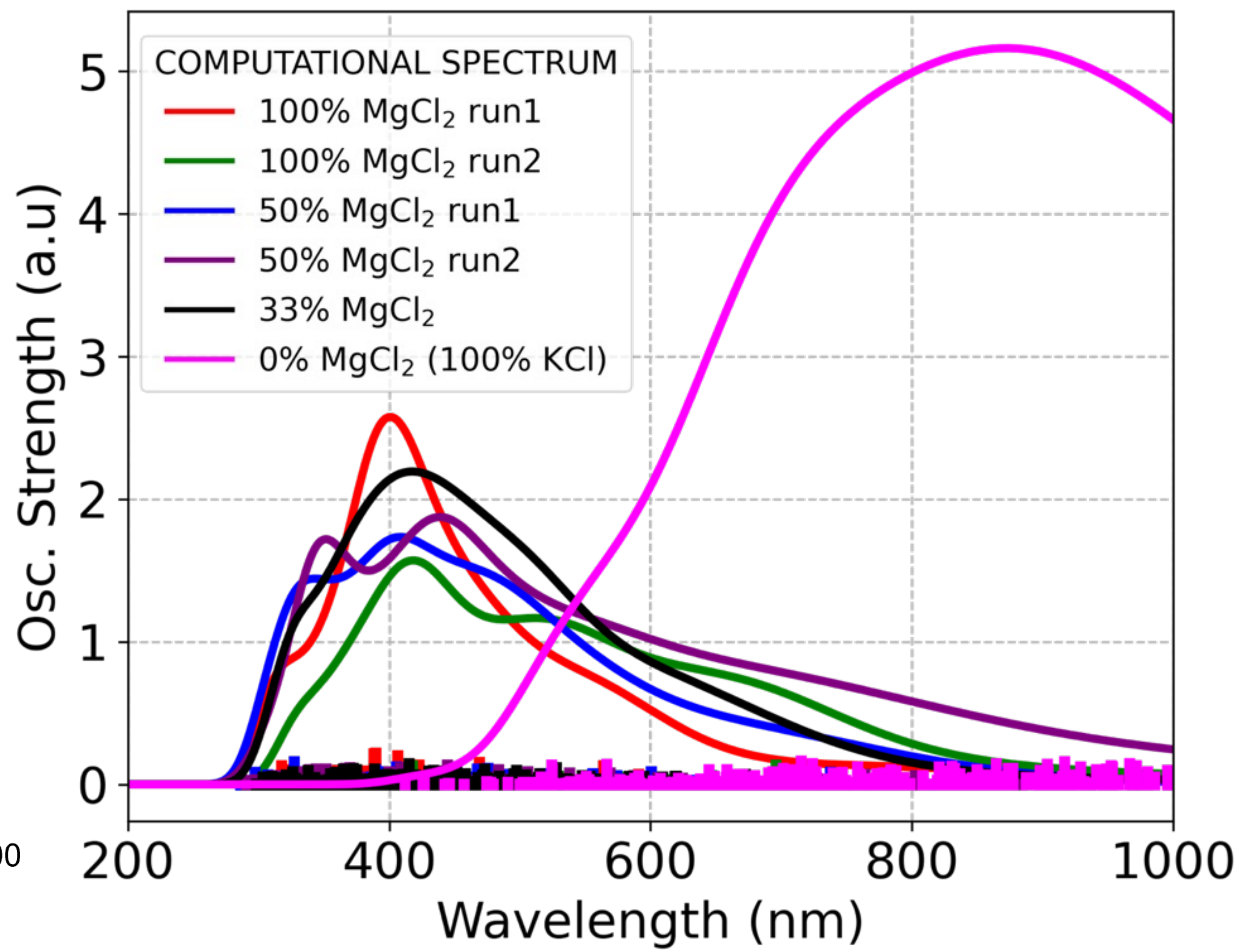
dimer



Hung Nguyen, Iowa

New: Ab initio MD simulations account for observed spectra of excess electrons in $MgCl_2$-KCl salt mixtures





Experimental radiolysis spectra by Kaz Iwamatsu. AIMD simulations by Hung Nguyen, Iowa

Solvated electron reactions with Co^{2+} and Zn^{2+} in different salt mixtures

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In eutectic LiCl-KCl

Metal ion	Occupancy	$k_{400\,°C}$ × 10^{10} M^{-1} s^{-1}	A × 10^{13} M^{-1} s^{-1}	E_a kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} deg^{-1}
Co^{2+}	d^7	5.8 ± 0.3	6.3 ± 0.7	39.1 ± 0.7	32.8 ± 1.3	**3.4 ± 1.8**
Zn^{2+}	d^{10}	4.2 ± 0.1	1.4 ± 0.1	32.7 ± 0.6	27.7 ± 0.5	**-8.5 ± 0.7**

In eutectic $MgCl_2$-KCl (32% $MgCl_2$)

Co^{2+}	d^7	3.3 ± 0.1*	0.59 ± 0.07	30.8 ± 1.6	22.0 ± 1.3	**-19.9 ± 1.6**
Zn^{2+}	d^{10}	1.2 ± 0.1*	0.19 ± 0.07	31.6 ± 1.2	24.8 ± 1.3	**-25.0 ± 1.6**

* @ 450 °C

In 50:50 $MgCl_2$-KCl

Co^{2+}	d^7	2.4 ± 0.2**	0.45 ± 0.07	33.3 ± 0.8	25.8 ± 0.9	**-20.4 ± 1.1**

** @ 500 °C

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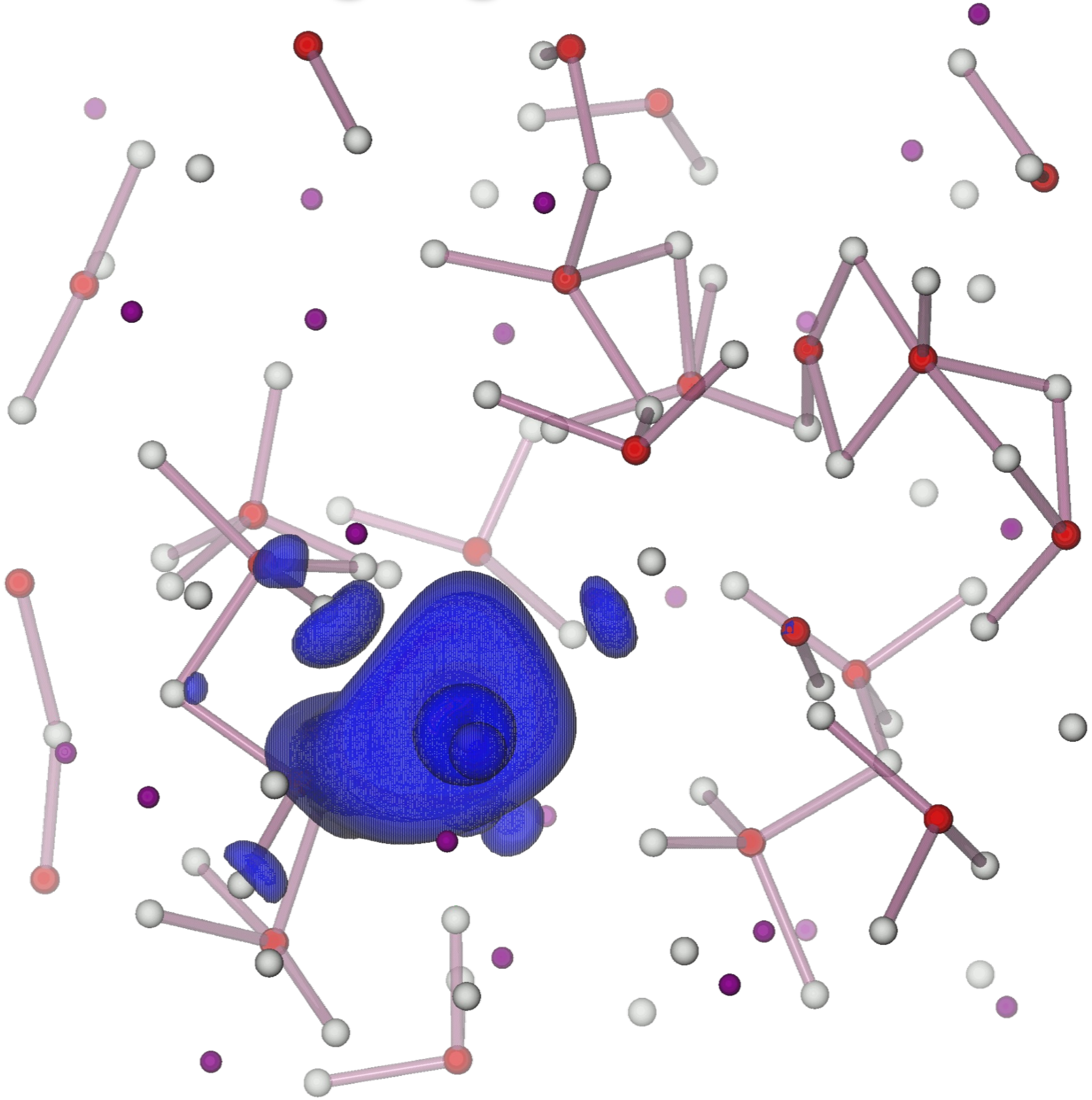
The electron can walk along Mg^{2+} networks

$50{:}50\ MgCl_2$-KCl

Red: Mg
Purple: K
Cl: white

Mg - Cl bond in pink
(bond cut off = 2.7 Å).

t = within 10 ps



Hung Nguyen, Iowa

Solvated electron reactivity influenced by metal ion coordination and identity

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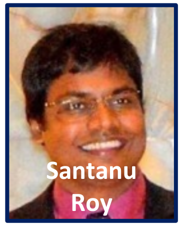
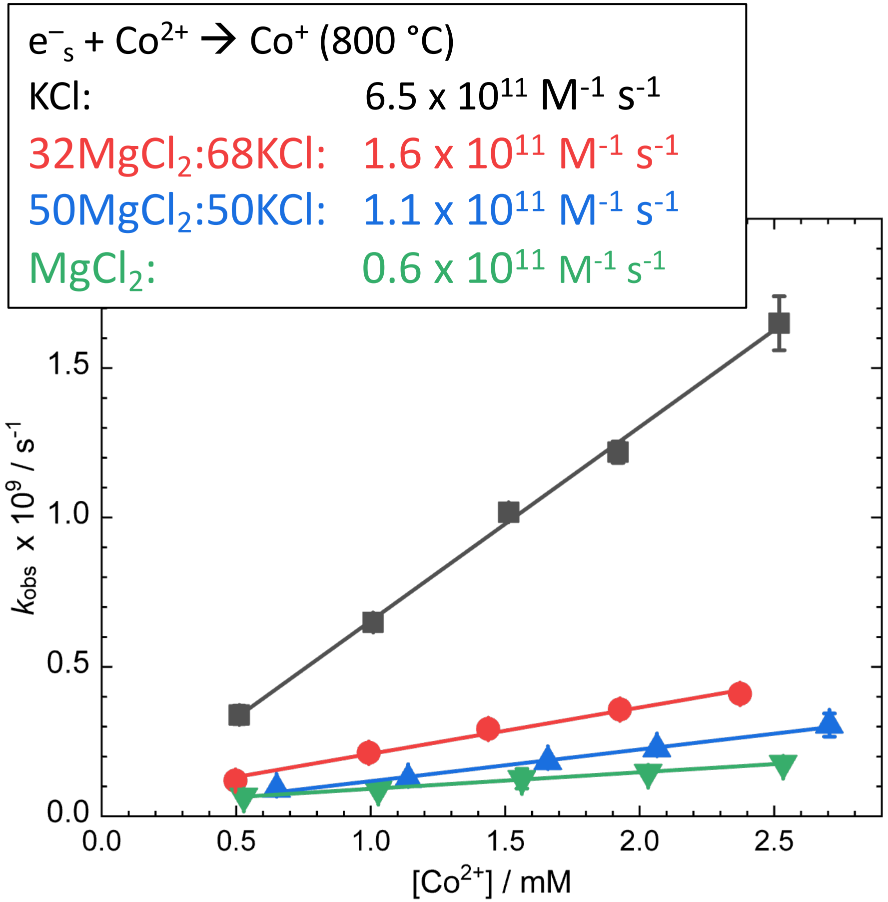
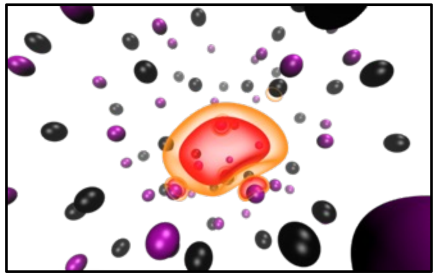


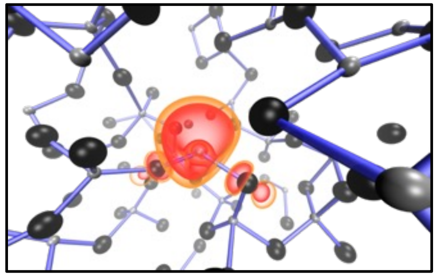
- Reactivity of the e_S^- with Co^{2+} decreases as the proportion of $MgCl_2$ in the solvent salt increases.
- Changes in chemical reactivity are correlated with the structure, mobility and chemical potential of the e_S^-.
- Ab initio MD simulations have revealed different interchanging forms of e_S^-.
- **Different solvation states afford changes in reactivity: $e_{K(cavity)}^- > e_{KMg}^- > e_{Mg}^-$.**



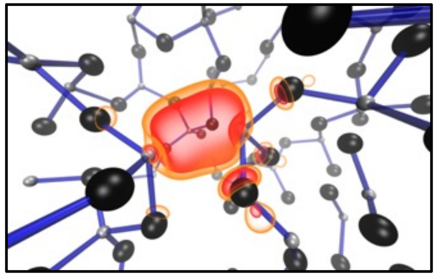
cavity e⁻



monomer



dimer



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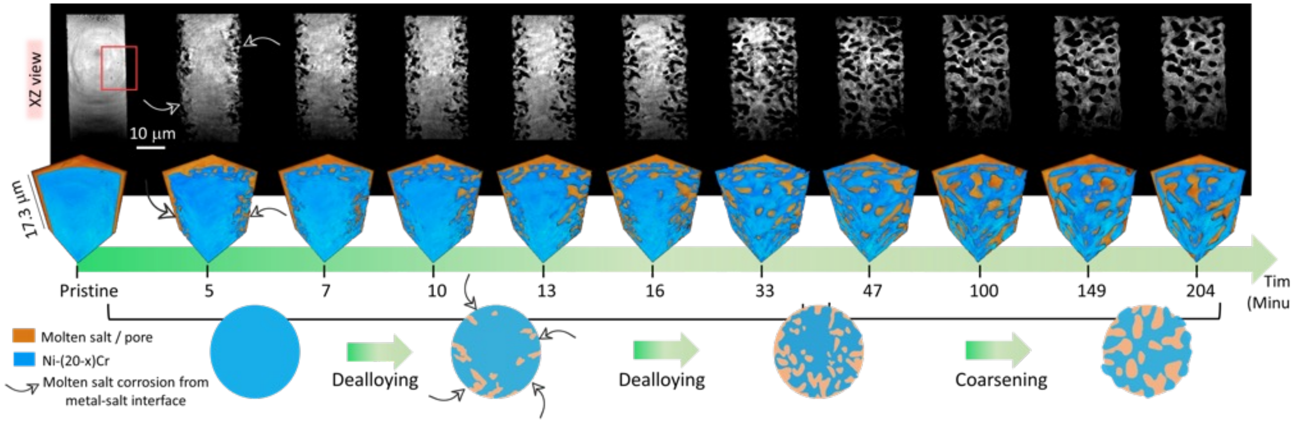
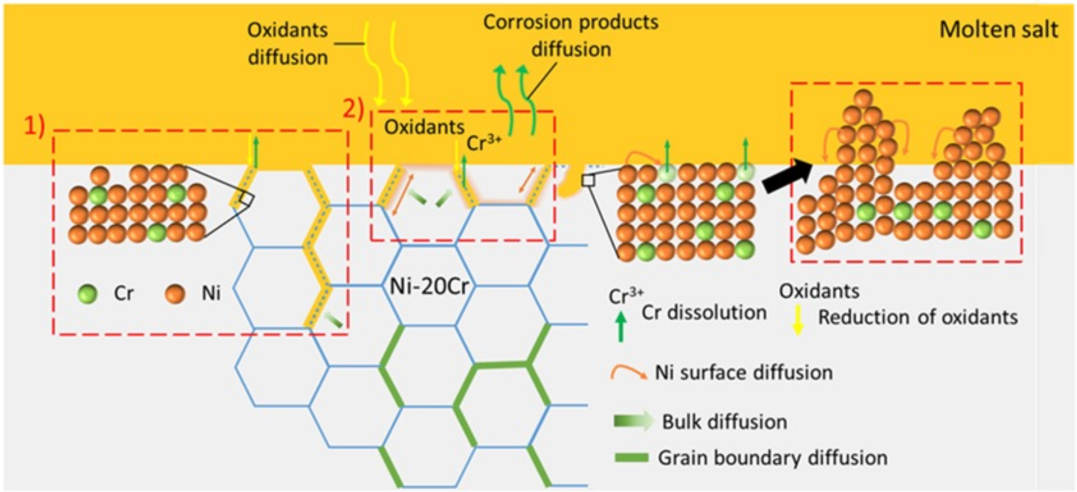
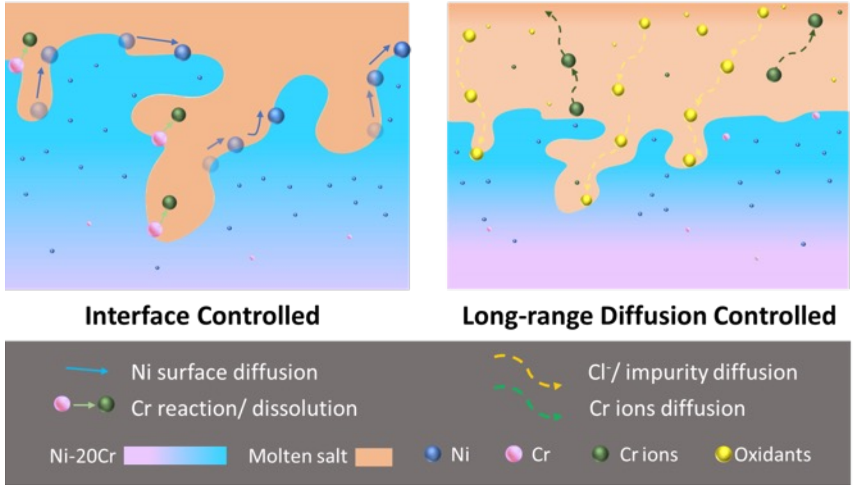
Fundamental processes governing interfacial morphological evolution

MSEE
molten salts in extreme environments







- **Competition between?**
  - Surface Diffusion of Ni
  - Chemical Reaction of Cr
- **Role of long-range diffusion?**
  - Vacancy in the solid-state
  - Oxidants and reaction products in the liquid state?

Four key factors:
(I) Temperature
(II) Oxygen and water
(III) Metal ions
(IV) Metallic species

Liu, Ronne, Chen-Wiegart, et al., Nature Communications (2021)

Liu, Chen-Wiegart, Bawane, Gakhar, Thornton, et al., ACS Applied Materials and Interfaces (2024)

Building molten salt capabilities at DOE facilities

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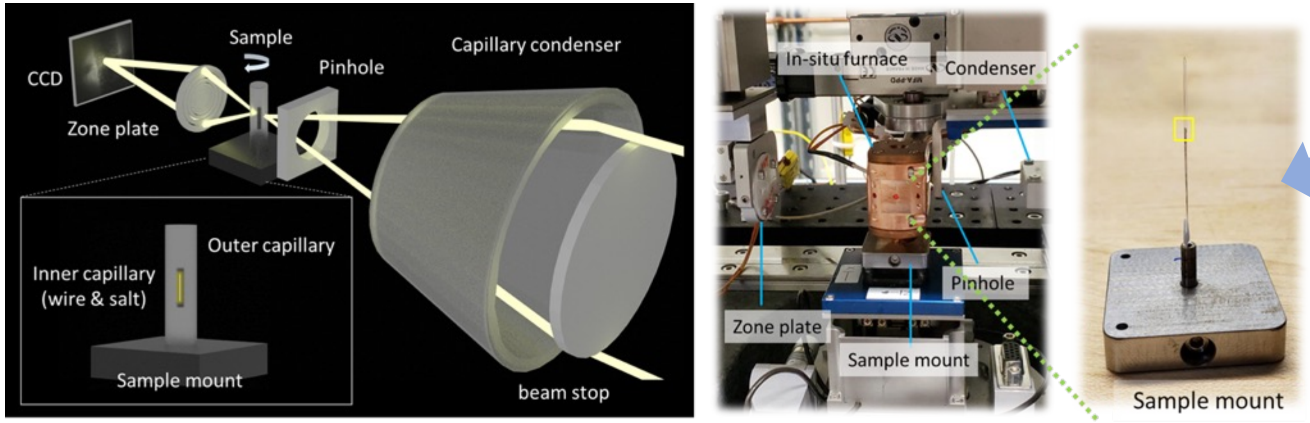
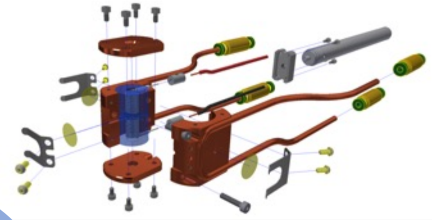
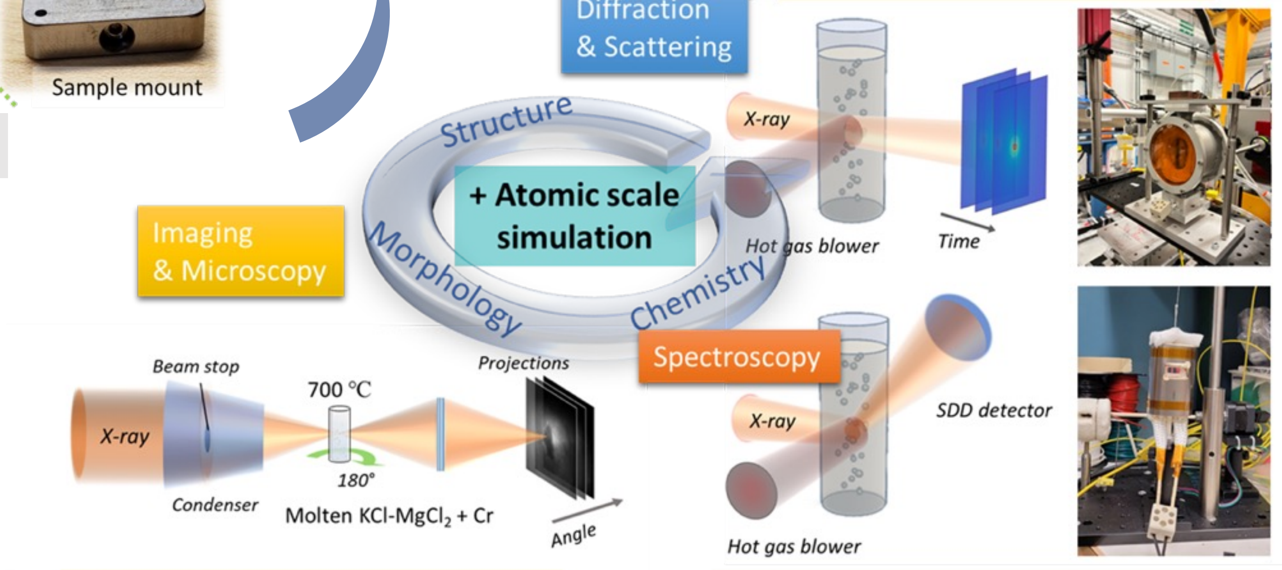


Full-Filed X-ray Imaging (FXI) Beamline, NSLS-II



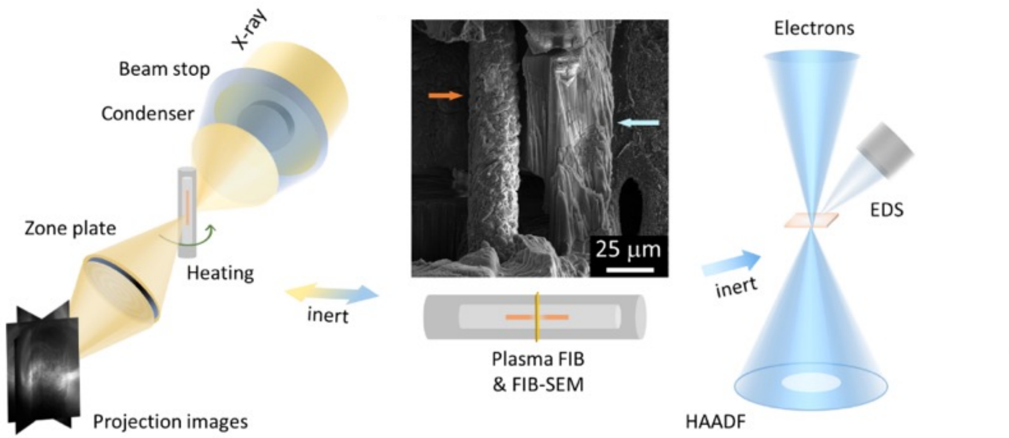
Antonelli, Ronne, Chen-Wiegart, Xiao, et al., Journal of Synchrotron Radiation, (2020)

X-ray powder diffraction (28-ID-1, PDF beamline)



Transmission X-ray microscopy (18-ID, FXI beamline)

X-ray absorption spectroscopy (8-ID, ISS beamline)



3D morphology by TXM at BNL + Elemental Mapping by STEM at INL

Liu, Bawane, Chen-Wiegart, et al., ACS Applied Materials & Interfaces (2023)

Liu, Chen-Wiegart, et al., Physical Chemistry Chemical Physics (2024)

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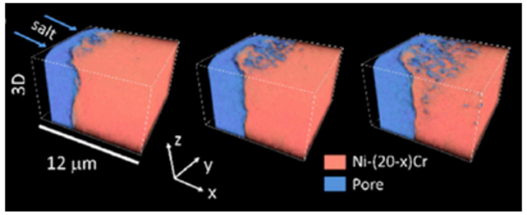
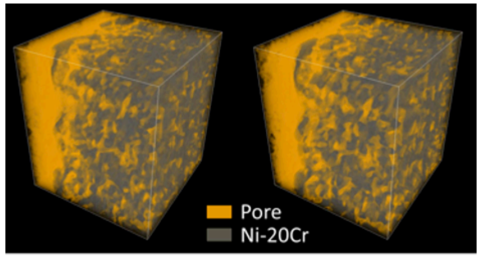
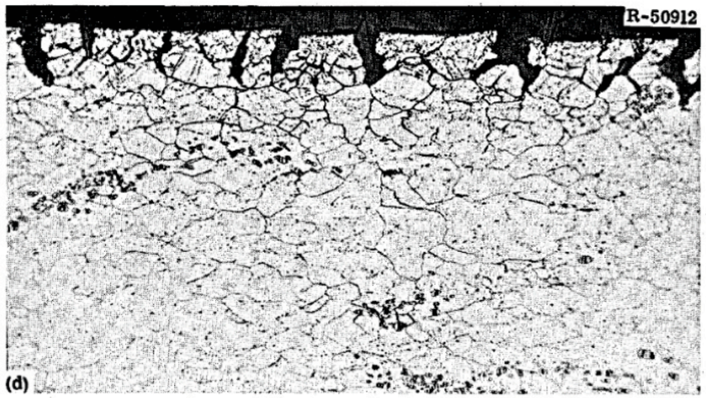
Key Factor (I) Temperature-dependent interfacial morphology
From dealloying to intergranular corrosion transition



500 °C

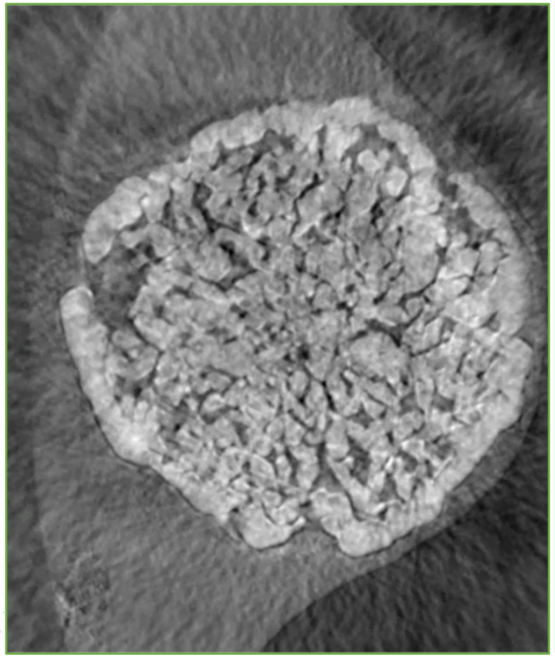


K Bawane et.al., Corrosion Sciences, (2021)



Intergranular Corrosion

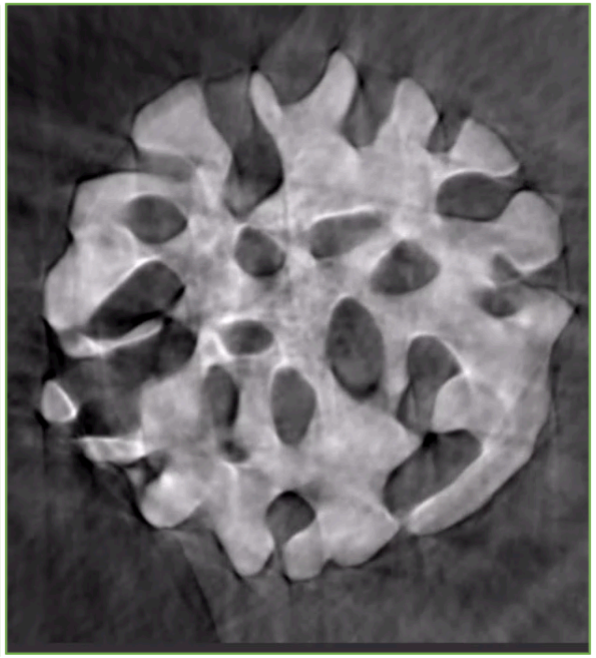
600 °C



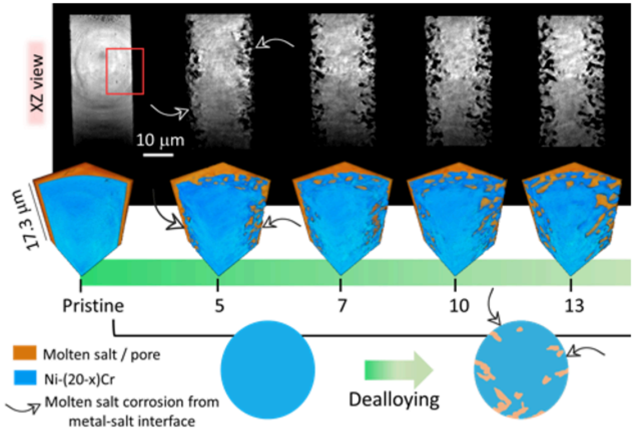
ORNL-4829, Report from Oak Ridge National Laboratory (ORNL), Molten Salt Reactor Experiment (MSRE)

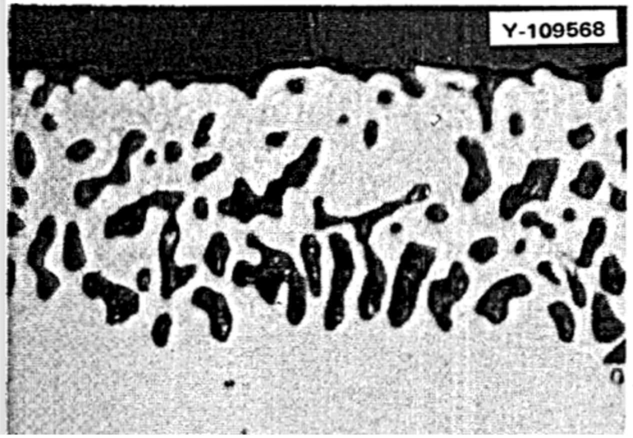
Percolation Dealloying

800 °C



ORNL-TM-4189, Report from ORNL, MSRE





Liu, Chen-Wiegart, et al., ACS Applied Materials & Interfaces (2023)

Liu, Ronne, Chen-Wiegart, et al., Nature Communications (2021)

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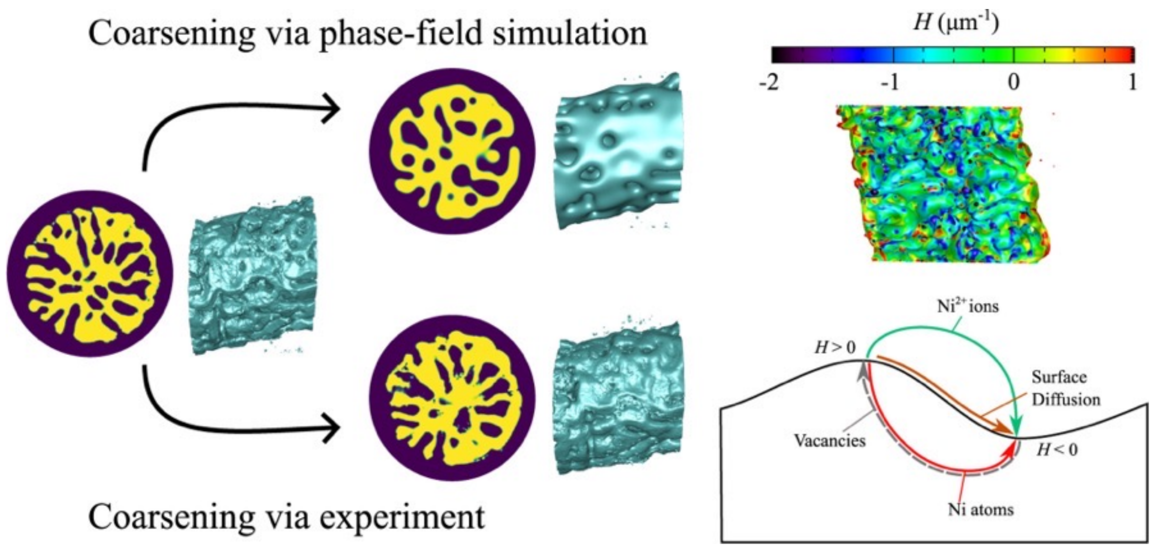
Phase-Field Modeling of Coarsening Mechanisms in Dealloyed Ni–Cr Microwires in Molten Salt

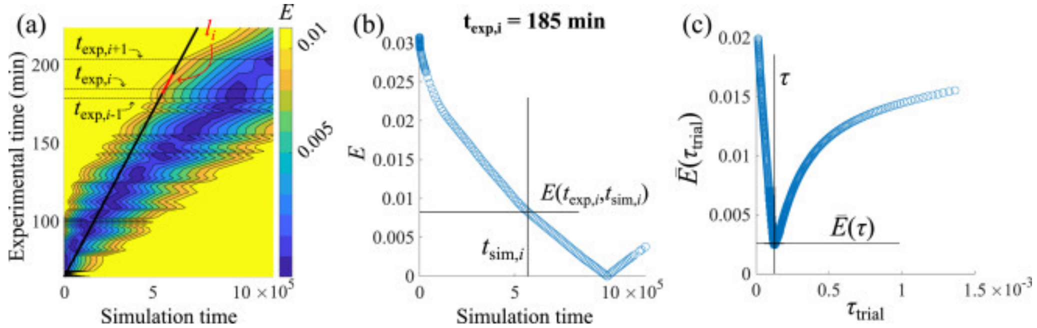


Katsuyo Thornton Ellery Hendrix W. Beck Andrews

MSEE molten salts in extreme environments

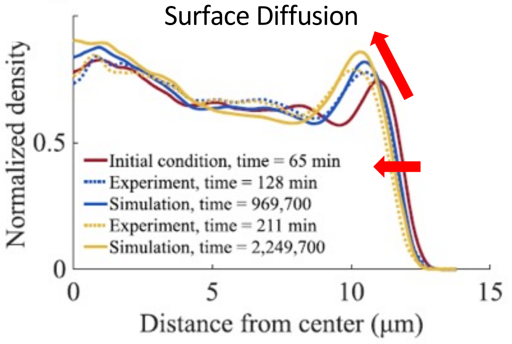
University of Michigan





Quantify the similarities and differences between predicted microstructures experimental data

- **Radial density function** provides a good measure for the comparison: densification and inward motion
- Matching enables comparison to kinetic parameters for similar systems



	B^{RDF}	B^{lit}
Surface diffusion (m^4/s)	1.51×10^{-28}	1.69×10^{-29}
Solid bulk diffusion (m^3/s)	7.50×10^{-23}	9.40×10^{-27}
Liquid bulk diffusion (m^3/s)	2.26×10^{-22}	1.38×10^{-34}

Ellery J Hendrix, W. Beck Andrews, Xiaoyang Liu, Karen Chen-Wiegart, Katsuyo Thornton, Acta Materialia (2025)

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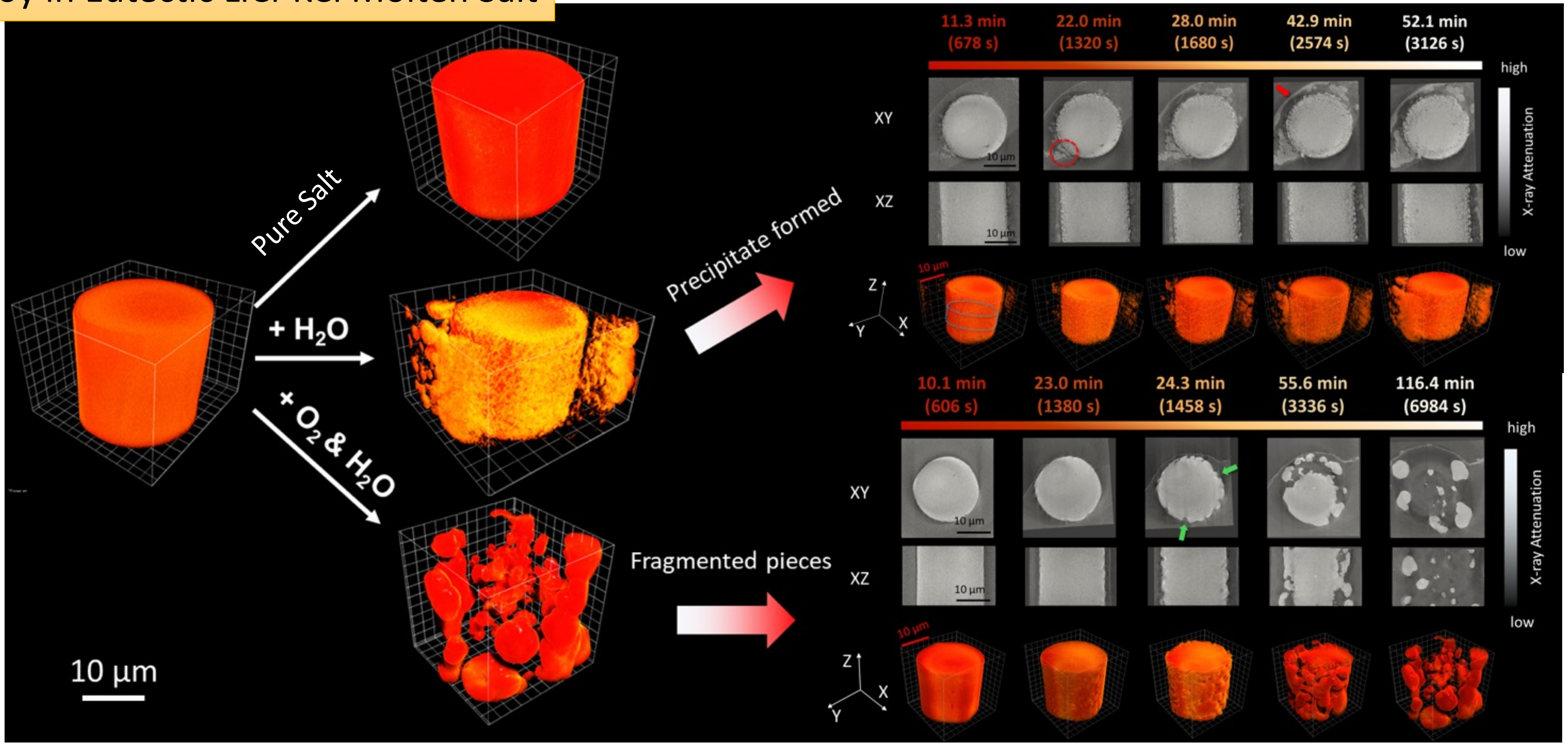
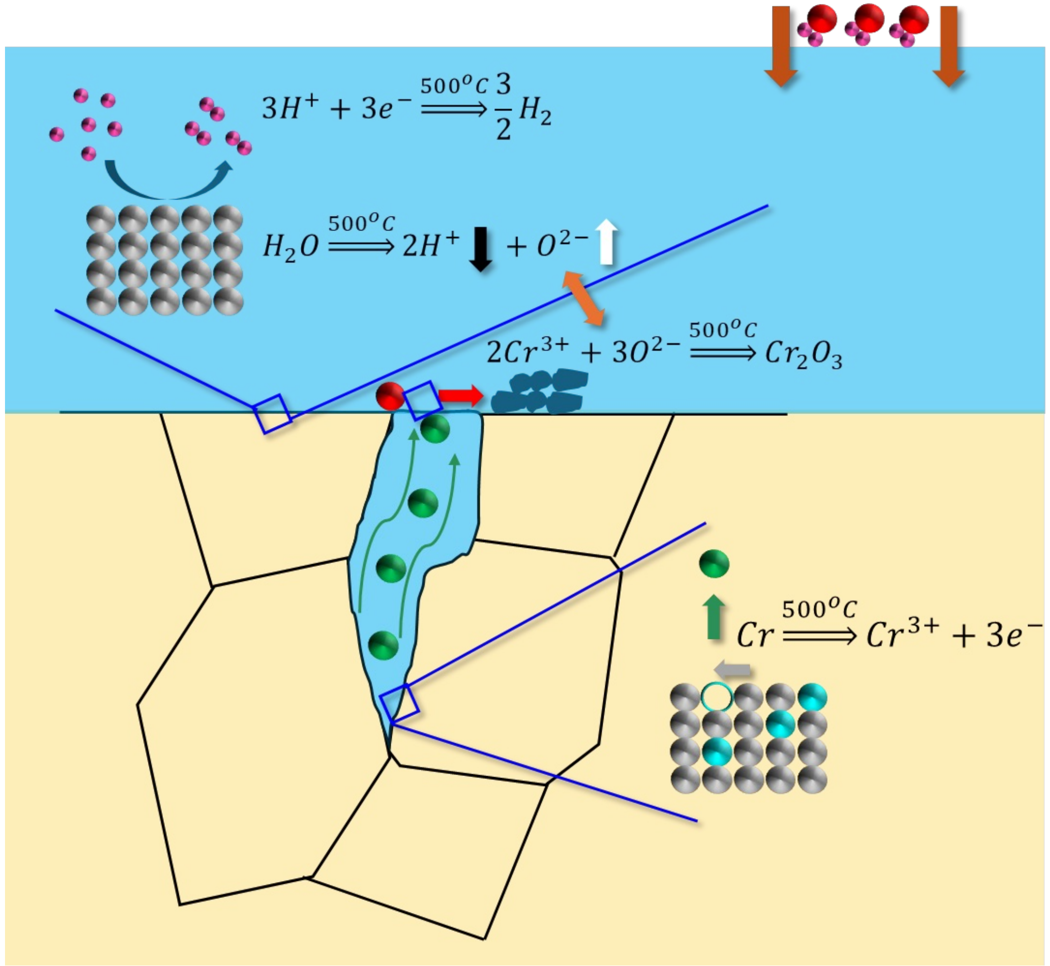
Key Factor (II) Oxygen and Water
Altering Corrosion Mechanisms and Microstructural Evolution

Ni–20Cr Alloy in Eutectic LiCl-KCl Molten Salt

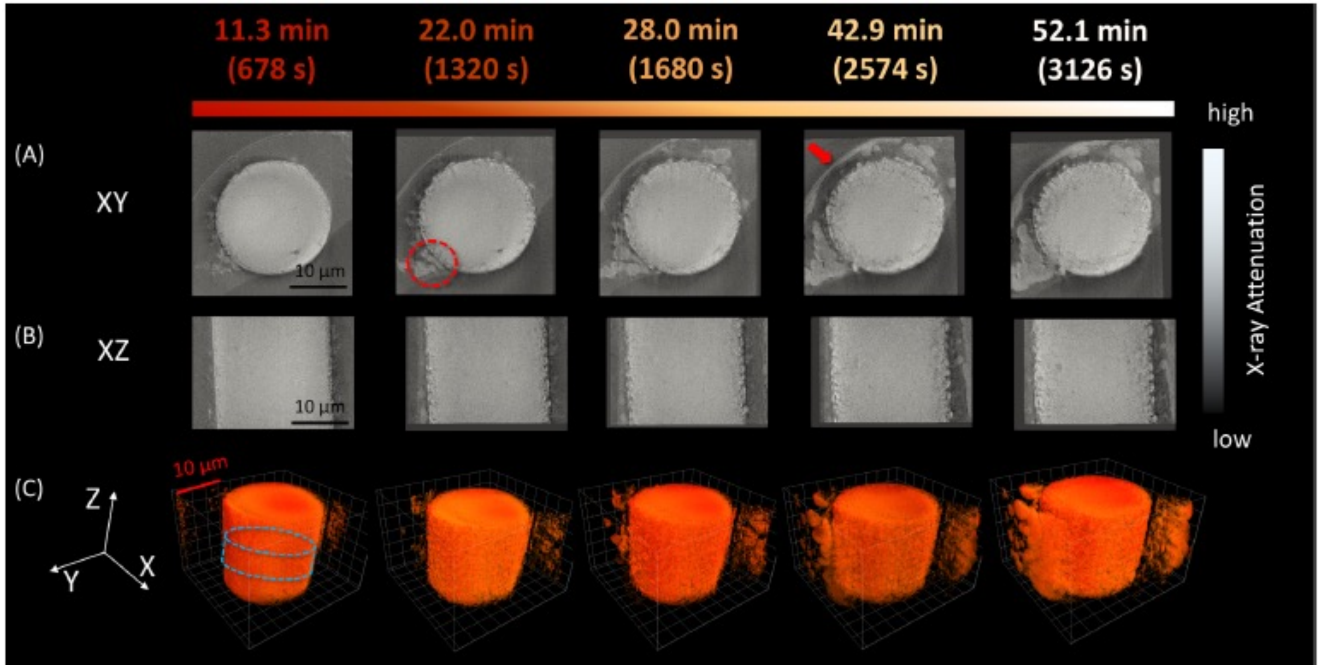


Yuxiang Peng, Kaustubh K. Bawane, Xiaoyang Liu, Xiaoyin Zheng, Mingyuan Ge, Xianghui Xiao, Ellie M. Kim, Phillip W. Halstenberg, Sheng Dai, James F. Wishart, and Yu-chen Karen Chen-Wiegart. *ACS Appl. Mater. Interfaces (2025)*

Key Factor (II) Water only



- **Key:** Cr reacted at the interface forming ions. The transport of the ions into the salt, forming oxides in the molten salt, not necessarily at the alloy interfaces



Yuxiang Peng, Kaustubh K. Bawane, Xiaoyang Liu, Xiaoyin Zheng, Mingyuan Ge, Xianghui Xiao, Ellie M. Kim, Phillip W. Halstenberg, Sheng Dai, James F. Wishart, and Yu-chen Karen Chen-Wiegart. *ACS Appl. Mater. Interfaces (2025)*

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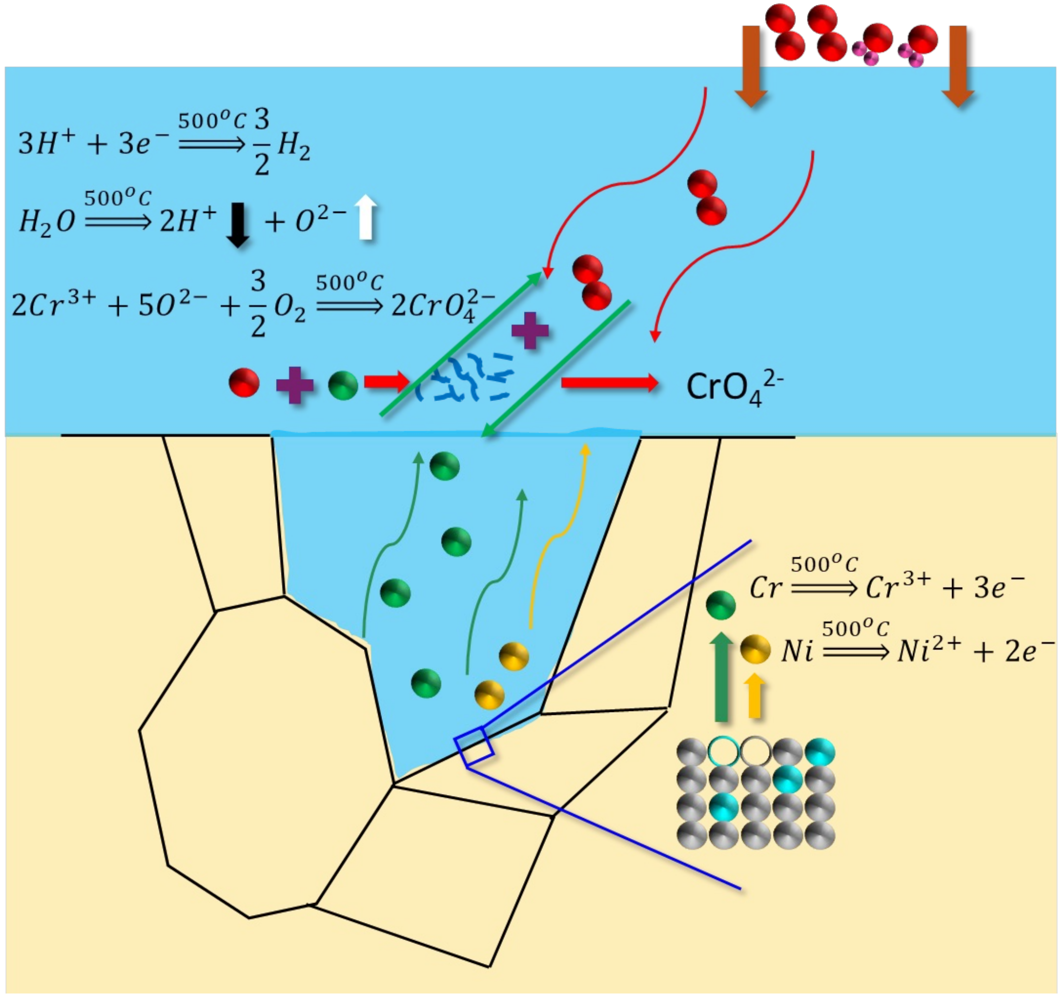
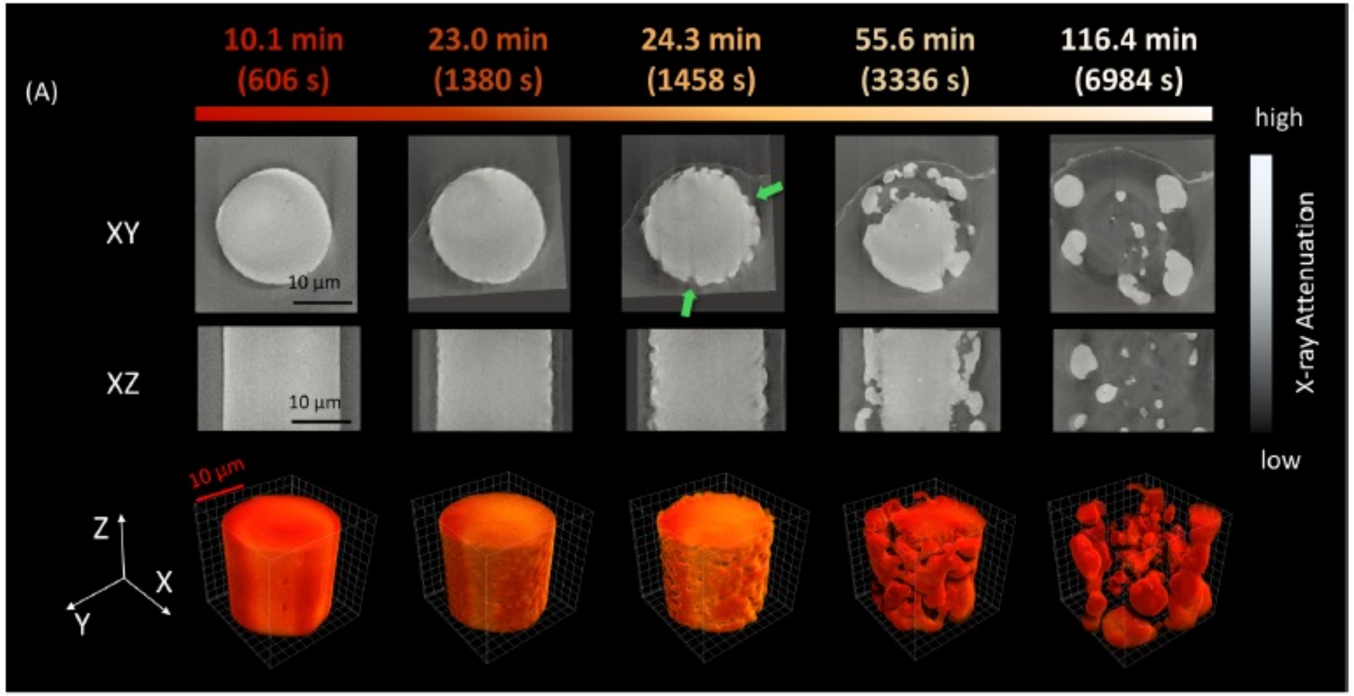
Key Factor (II) Both H_2O and O_2 impurity



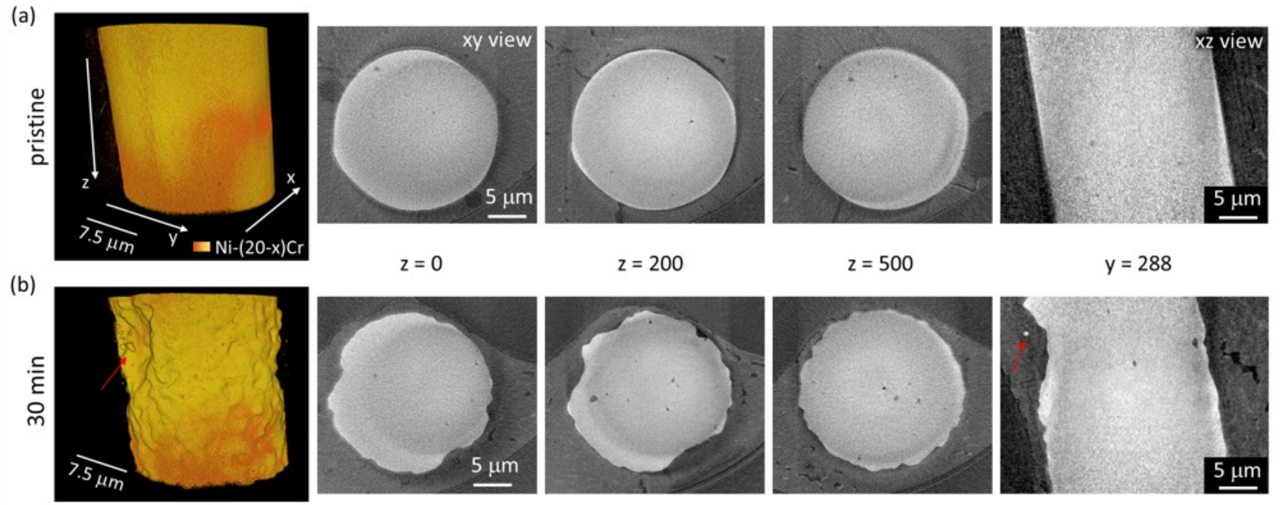


Yuxiang Peng, Kaustubh K. Bawane, Xiaoyang Liu, Xiaoyin Zheng, Mingyuan Ge, Xianghui Xiao, Ellie M. Kim, Phillip W. Halstenberg, Sheng Dai, James F. Wishart, and Yu-chen Karen Chen-Wiegart. *ACS Appl. Mater. Interfaces (2025)*

Key Factor (III) Metal Chlorides: Fission Products
From planar corrosion to mixed characters of corrosion front

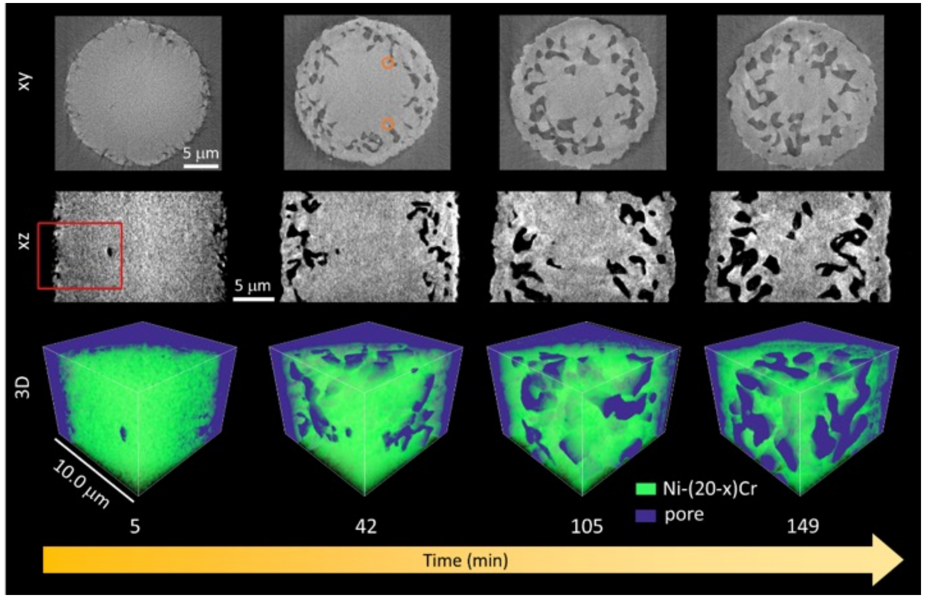
Redox couple	Ce(III)/Ce	Cr(II)/Cr	Ni(II)/Ni	Eu(III)/Eu
Redox potential (vs. Cl_2/ Cl^-)	-2.96 V	-2.0 V	-1.3 V	-0.66 V

Ni-20Cr in molten KCl-$MgCl_2$ (50-50 mol.%) **at 700 ℃**



with 1 wt.% $CeCl_3$

Surface/planar corrosion



with 1 wt.% $EuCl_3$ at 700 ℃

Mixed intergranular attacks and dealloying

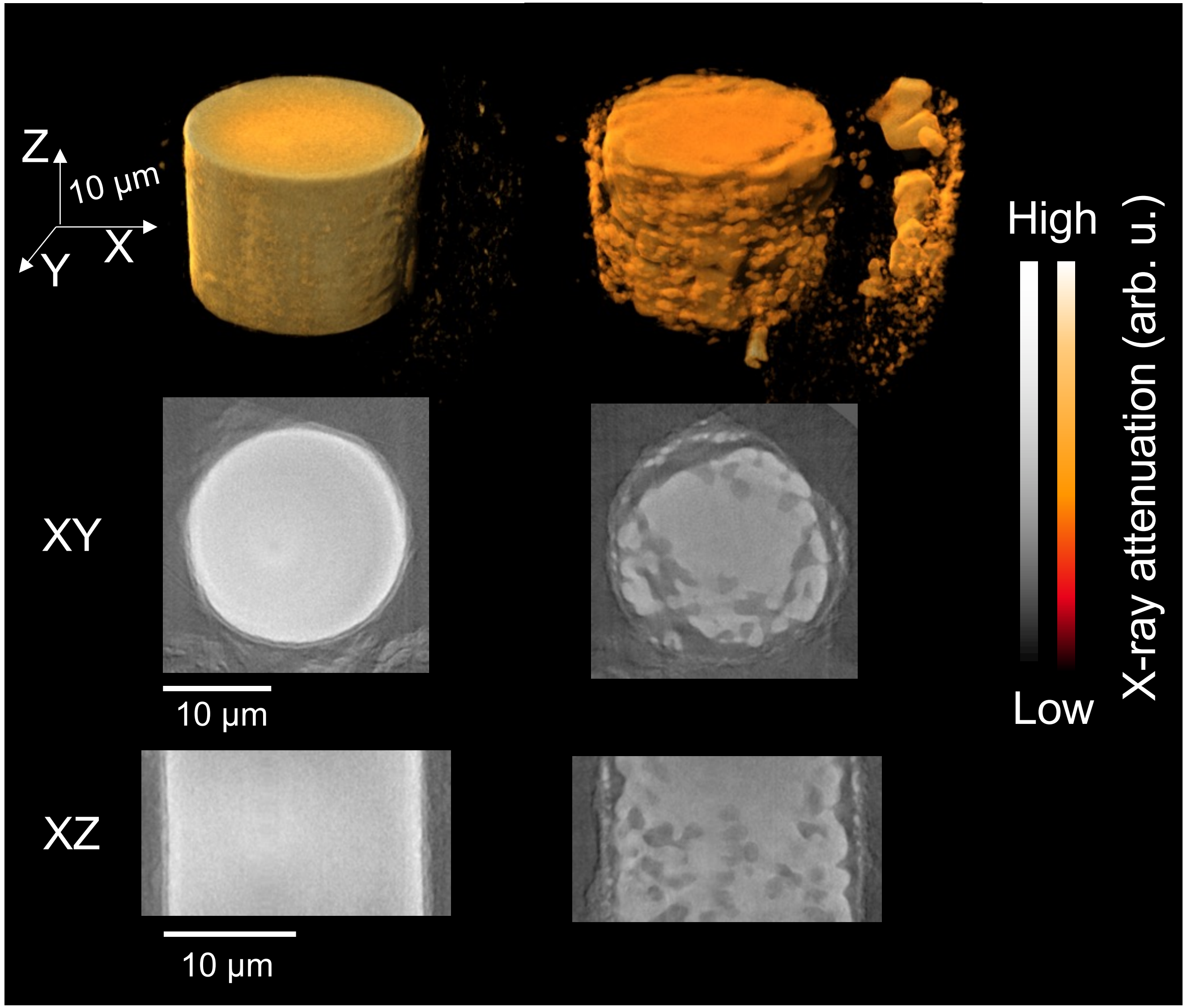
Liu, Chen-Wiegart, Bawane, Gakhar, Thornton, et al., ACS Applied Materials and Interfaces 2024

Key Factor (IV) Metallic species Ongoing work

- **Effects of metals:** Quantifying how corrosion-control metals and metallic fission products (e.g., Zr, Te) influence intermetallic phase formation and interfacial changes of structural alloys in molten salts.

Dr. Yuxiang Peng

Stony Brook University



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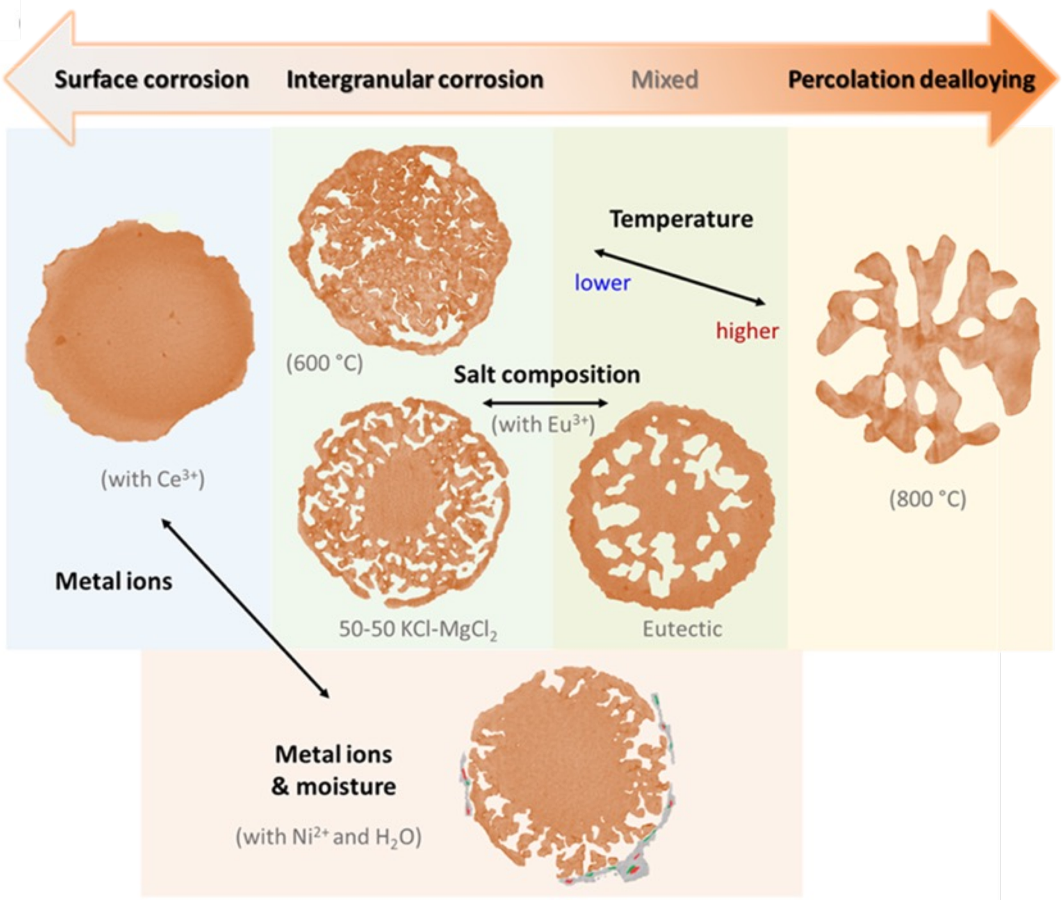
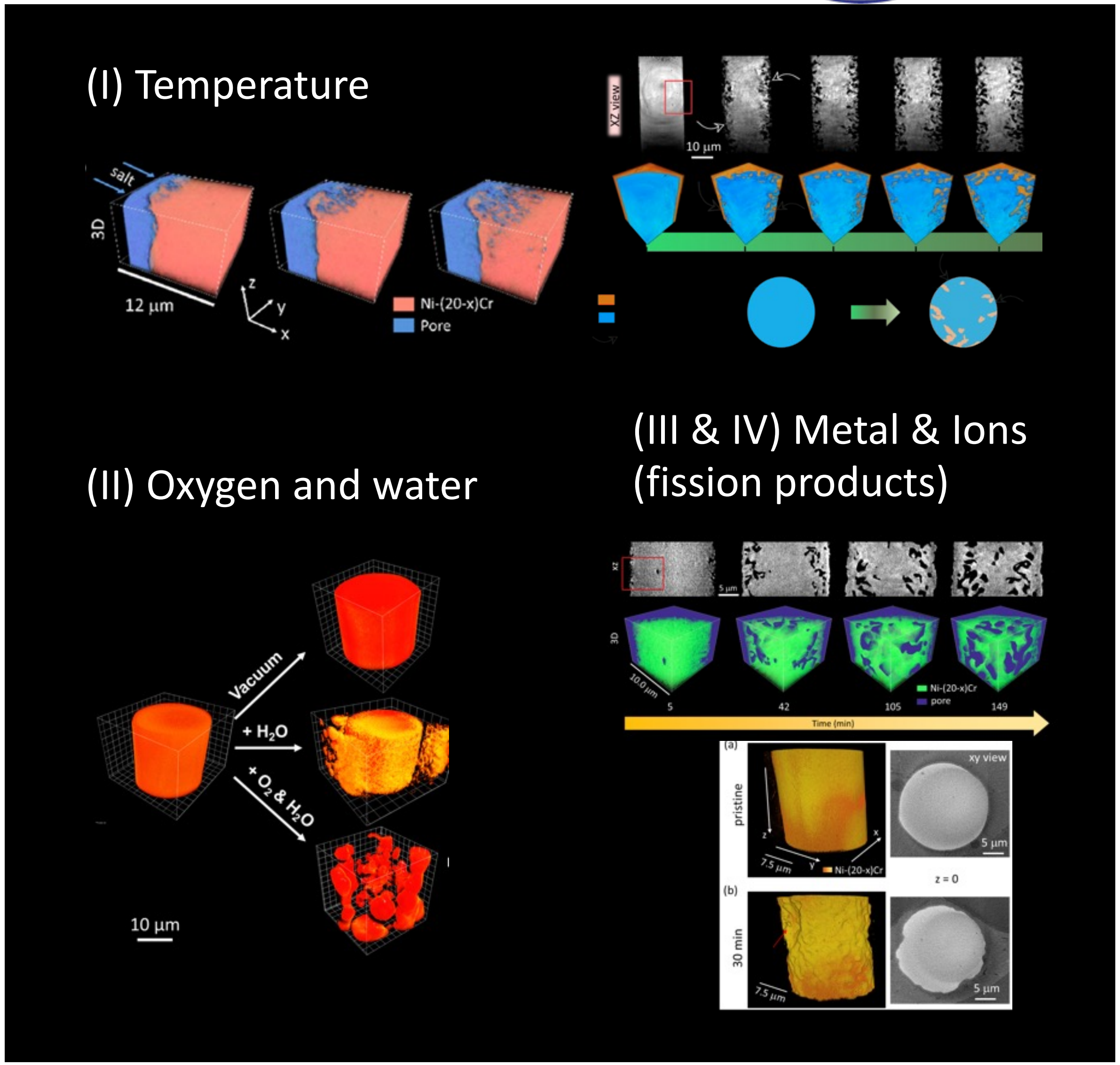
Towards a 'phase diagram' for morphological evolution

MSEE molten salts in extreme environments



Liu, Chen-Wiegart, Bawane, Gakhar, Thornton, et al., ACS Applied Materials and Interfaces (2024)



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Acknowledgments

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All MSEE PIs, Staff, Postdocs and Graduate Students

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