INL/CON-25-83799-Revision-0

In situ Monitoring of Lanthanide Reactions with Oxide Species via Combined Absorption Spectroscopy and Electrochemical Methods

May 2025

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Idaho National Laboratory

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U.S. Department of Energy's Office of Nuclear Energy

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O^{2-} reacts with Lanthanides to form insoluble products in chloride-based molten salts

O^{2-} reacts with lanthanides (Ln) or actinides to form insoluble oxides or oxychlorides

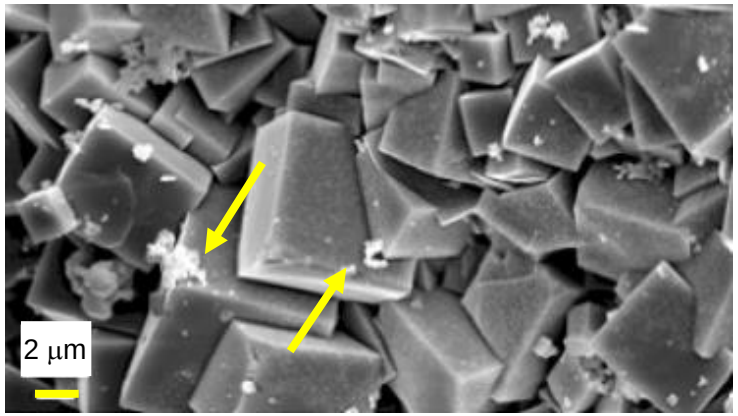
- Ln generally thought to form oxychlorides
- Temperature and lanthanide dependent[1,2]

$$LnCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons LnOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

$$LnCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Ln_2O_{3(s)} \downarrow + 3LiCl_{(l)}$$

Two key interests in reactions of species with O^{2-}

1. Oxygen impurities are ever-present
   - Molten salt reactor (MSR) operation changes with precipitate formation
   - Precipitate formation removes fuel and fission products
2. Metallic lanthanide/actinide products can be converted into easily separable oxides[3-4]

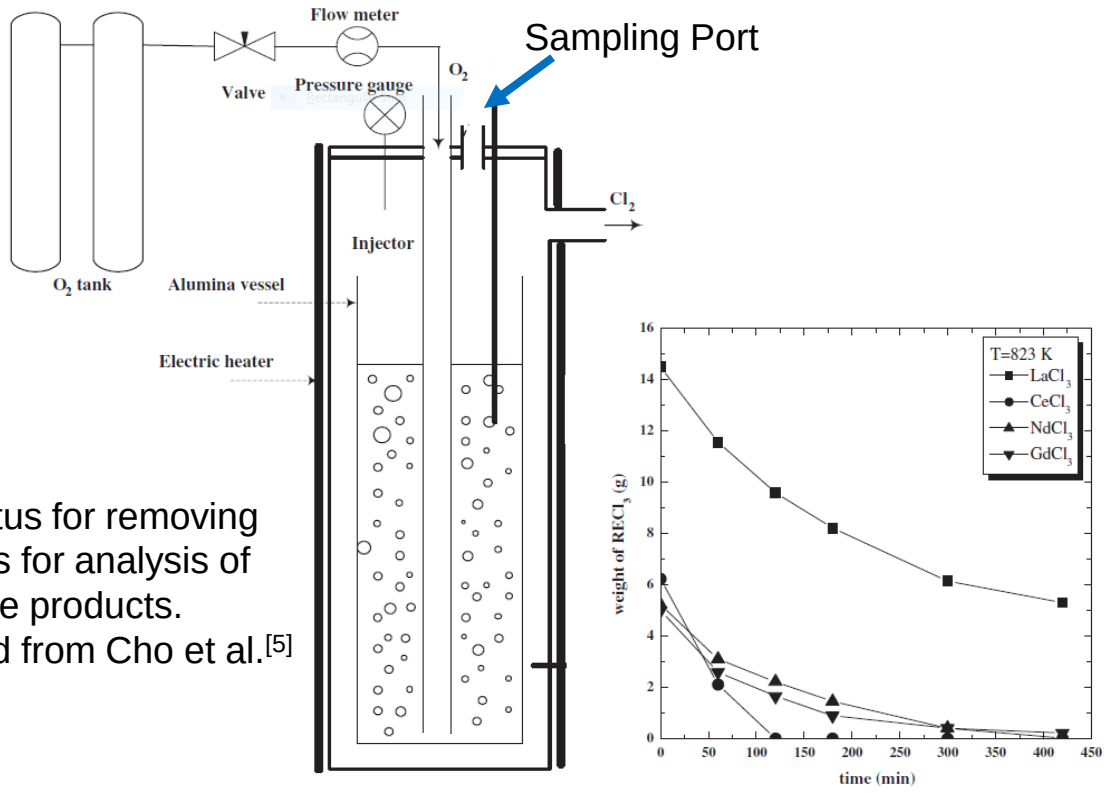


Example of oxide or oxychloride precipitates in LiCl-KCl (eut). Image adapted from Cho et al. [2]

[1] Y. Katayama, et al., Journal of The Electrochemical Society **142, 2174 (1995).**
[2] Y.-Z. Cho, et al., Journal of Nuclear Materials **384, 256 (2009).**
[3] H. C. Eun, et al., Journal of Nuclear Materials **408, 110 (2011).**
[4] V. A. Volkovich, et al., Journal of The Electrochemical Society **168, 046513 (2021).**

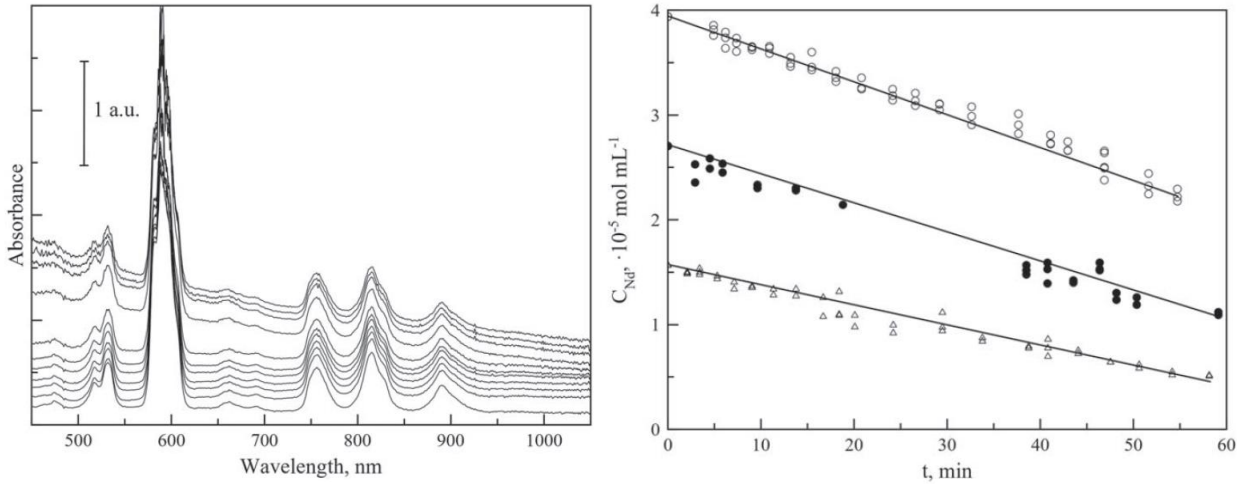
Online sampling and absorption spectroscopy have been used to track reaction kinetics/conversions

Extract samples during oxygen sparging[5]



Apparatus for removing samples for analysis of insoluble products. Adapted from Cho et al.[5]

High-temperature absorption spectroscopy[4]

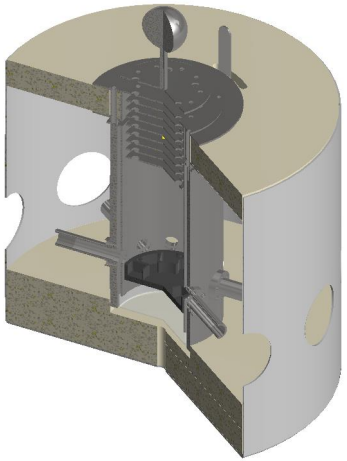


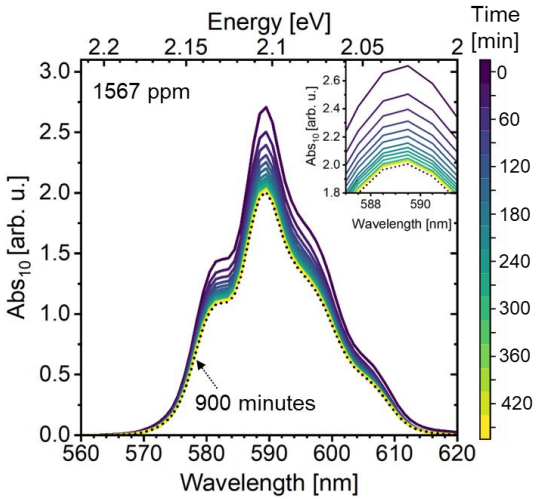
Absorption spectra of the reaction of Nd^{3+} with sparged O_2(g) and concentration of Nd^{3+} with time. Adapted from Volkovich et al.[4]

[4] V. A. Volkovich, et al., Journal of The Electrochemical Society **168, 046513 (2021).**

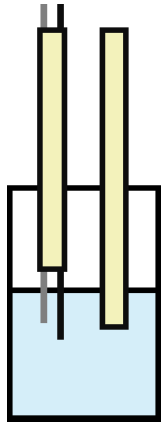
[5] .Y-J. Cho, et al., Journal of Nuclear Science and Technology **43, 1280 (2006).**

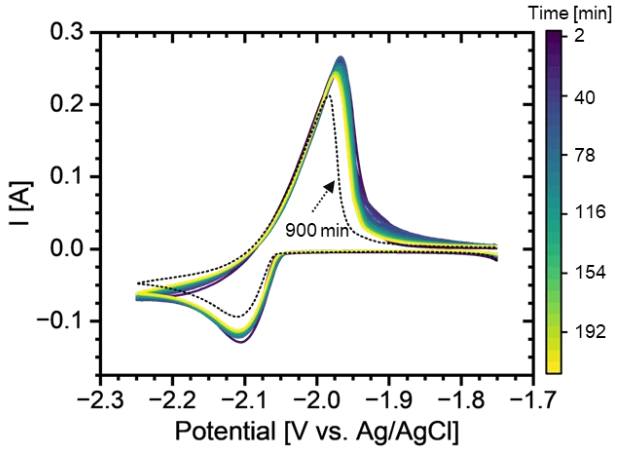
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy





Track reaction of Pr^{3+} with O^{2-} using both absorption spectroscopy and electrochemistry

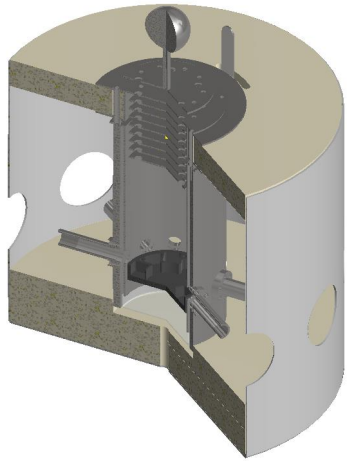


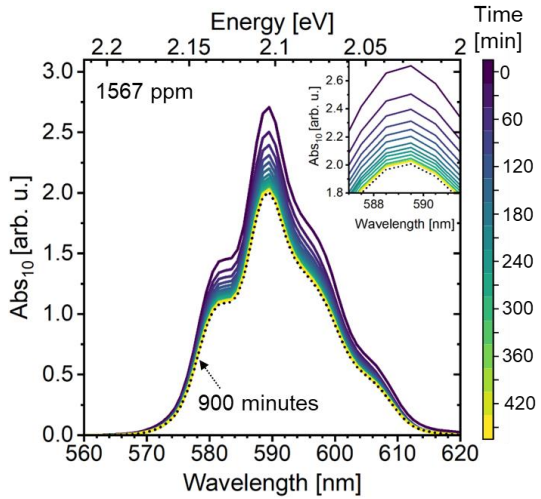


Techniques provide real-time clues

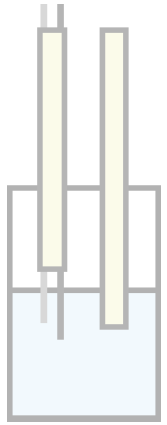
1. **reaction kinetics**
2. **product conversion**
3. **product formation (oxide/oxychloride)**

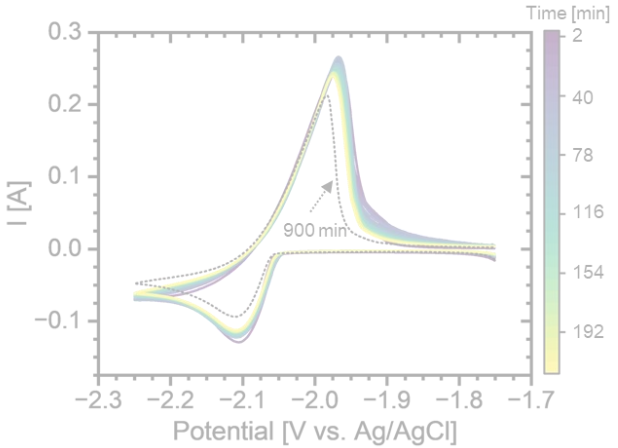
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy





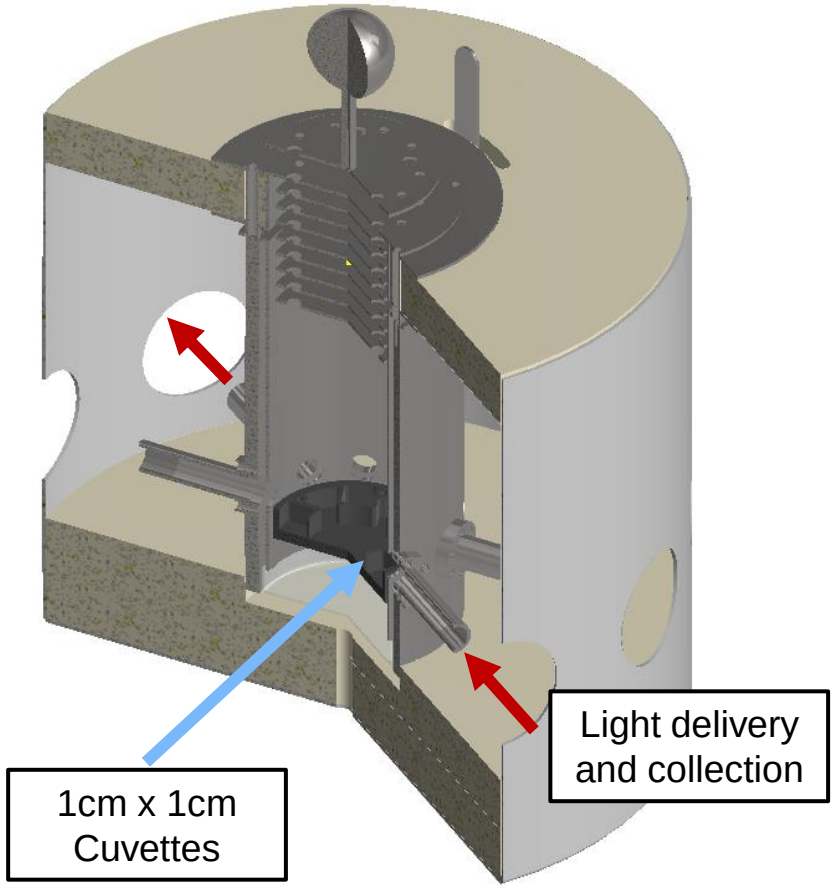
Track reaction of Pr^{3+} with O^{2-} using both absorption spectroscopy and electrochemistry



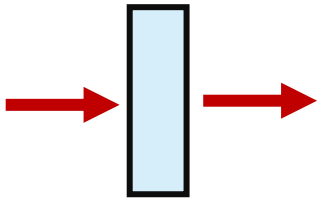


Tracking concentrations: spectroscopy

High-temperature transmission setup

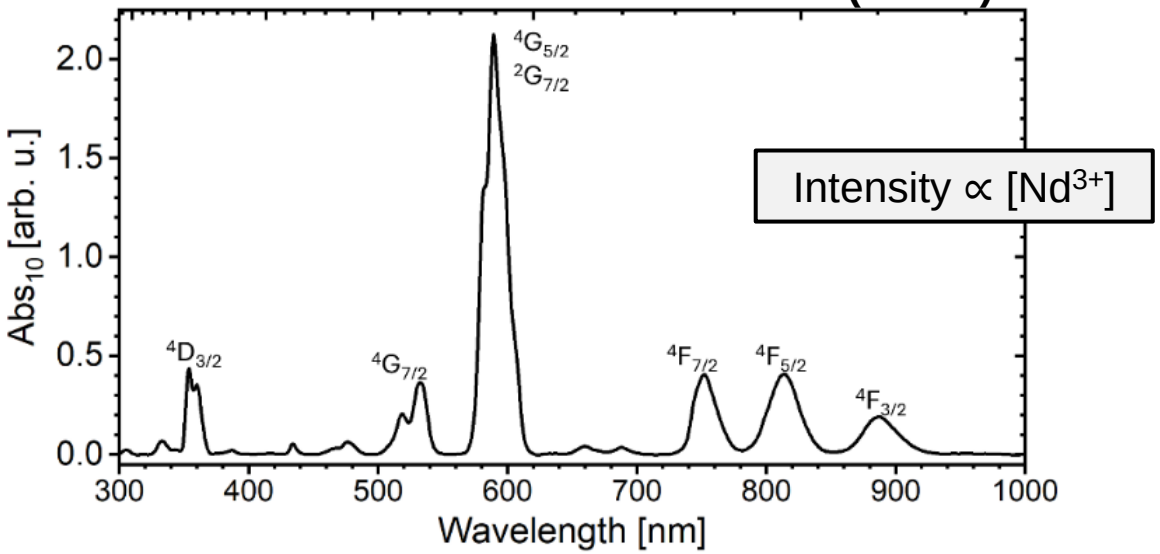


Transmission allows concentration monitoring



$$\text{Abs}_{10} = -\log_{10}(T) = \varepsilon L c$$

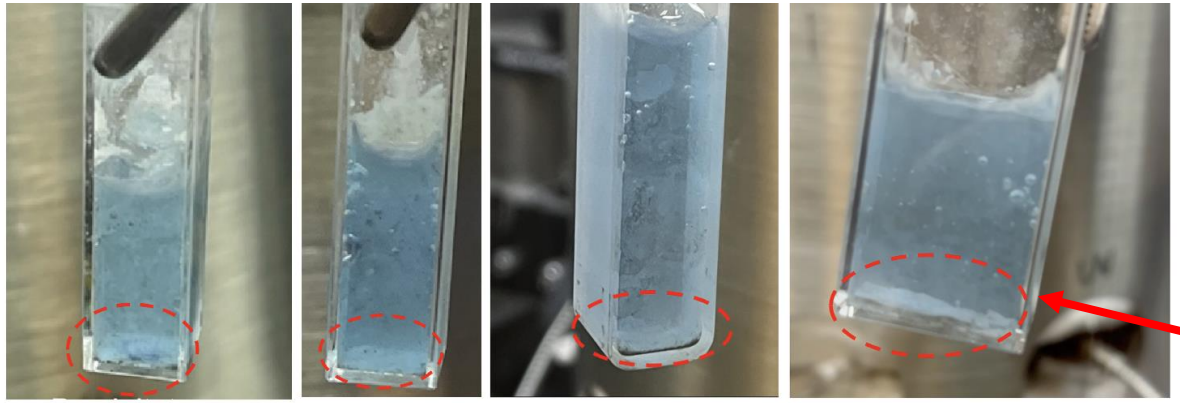
Nd^{3+} in LiCl-NaCl-KCl eutectic (500°C)



Oxide or oxychloride precipitates form after Li_2O addition

Add Li_2O to solutions of Nd^{3+} in LiCl-NaCl-KCl eutectic salt

24 ppm 66 ppm 152 ppm 1567 ppm



Precipitates form: Nd_2O_3 or NdOCl

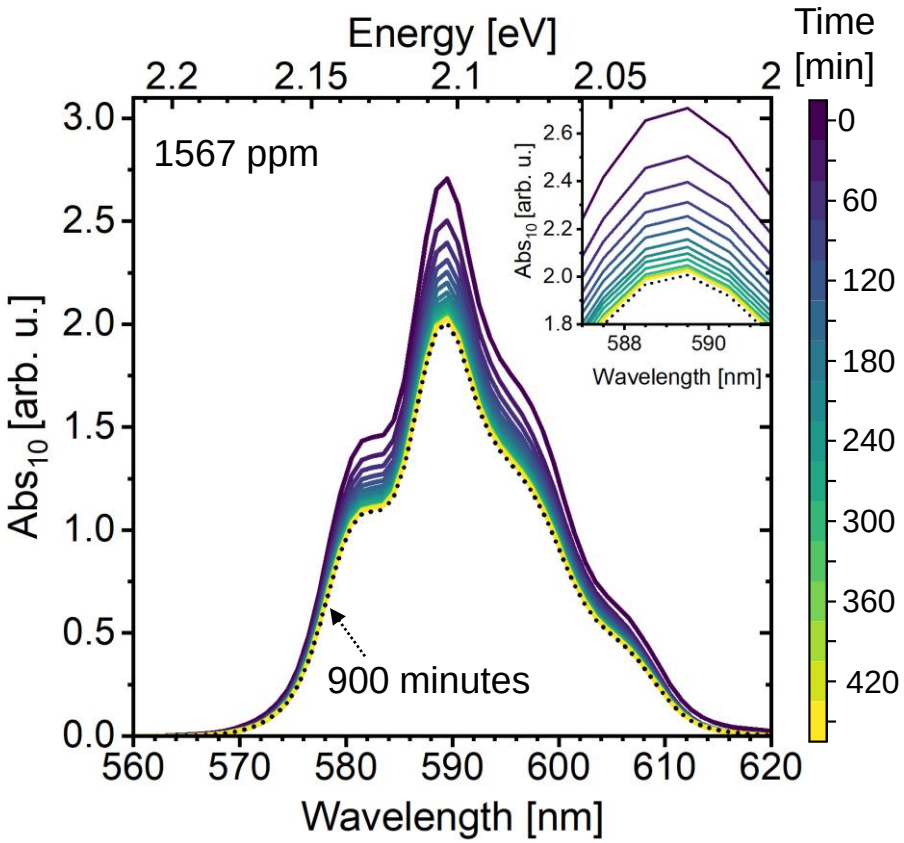
- Controlled addition of O^{2-} impurities
- Nd products precipitate out of solution
- Yields *loss* of Nd^{3+} absorbance intensity

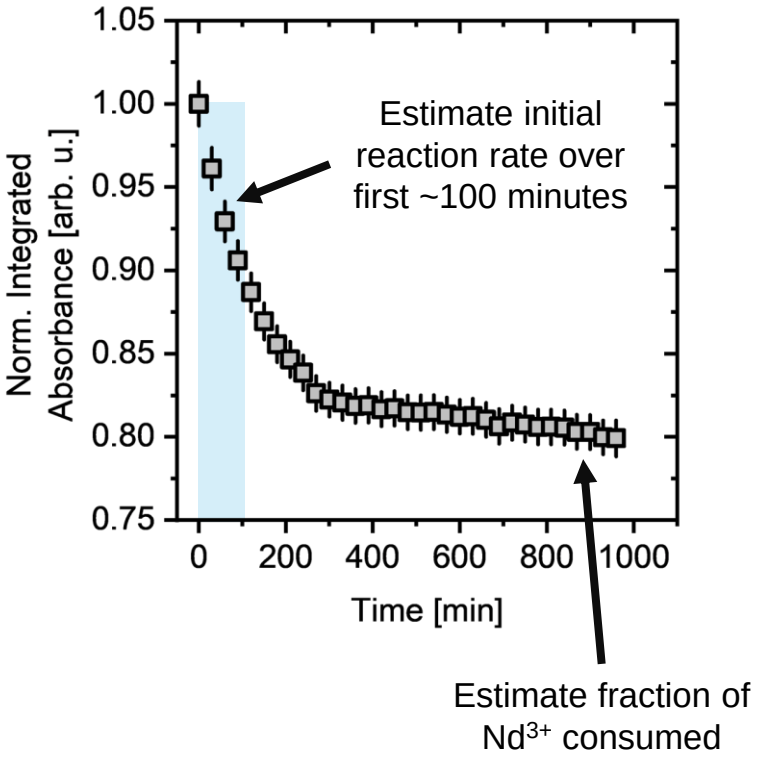
$$NdCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons NdOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

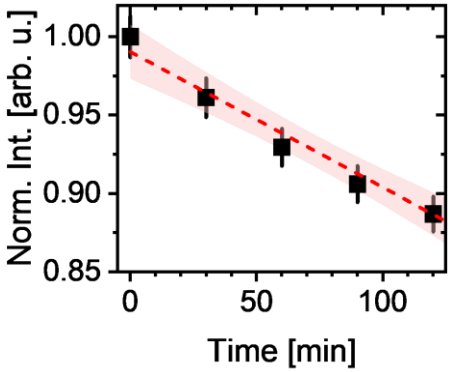
$$NdCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Nd_2O_{3(s)} \downarrow + 3LiCl_{(l)}$$

Can we use absorption spectroscopy to track the rates and conversions of these reactions?

[Nd^{3+}] decreases with time after adding Li_2O: What information does absorption spectroscopy yield?





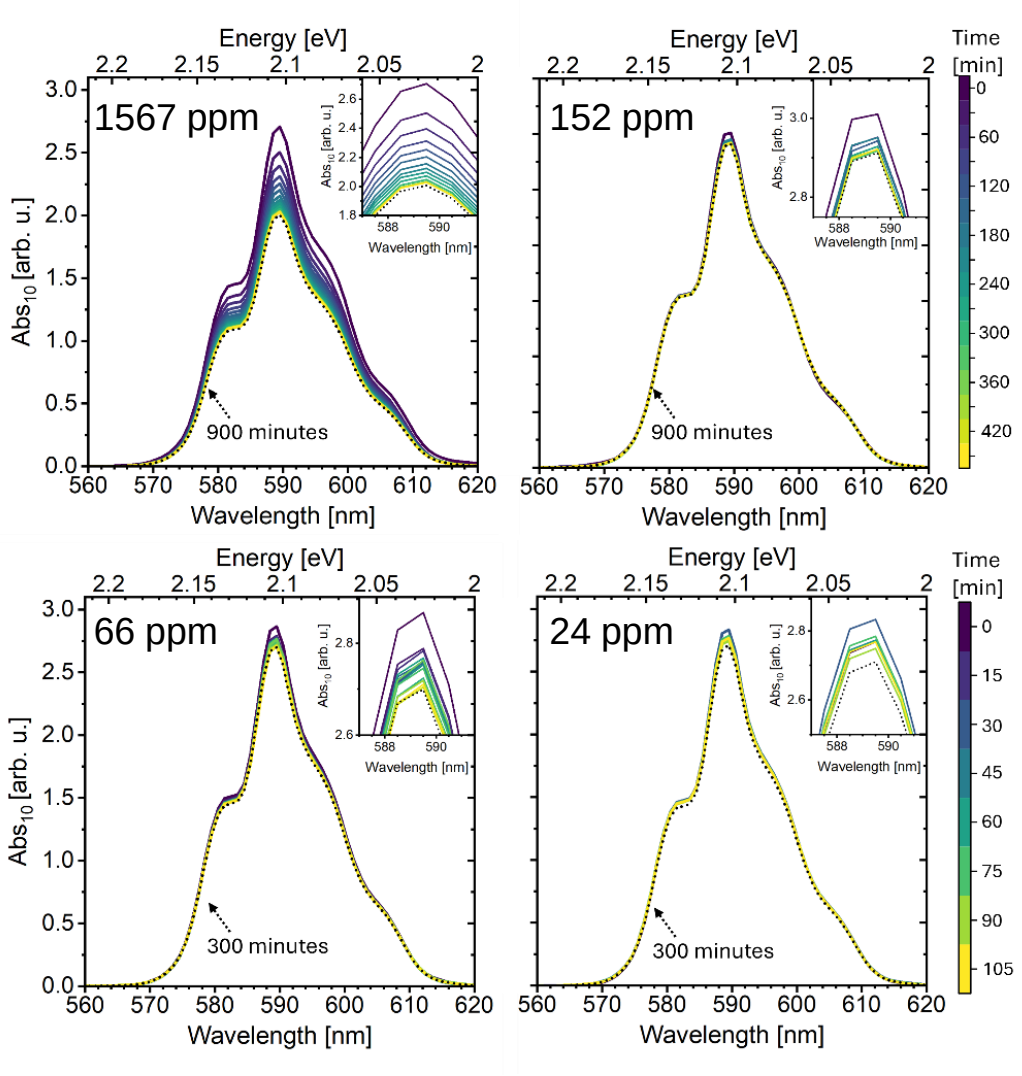


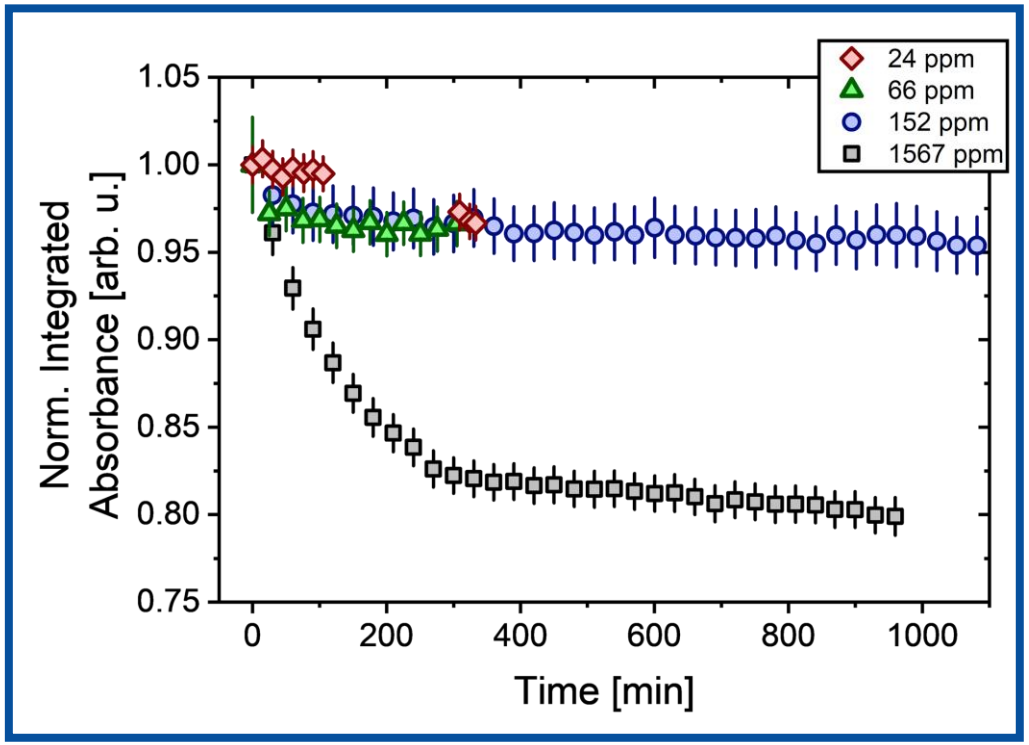
$$[Nd^{3+}](t) = \frac{Abs_{max}(t)}{Abs_{max}(0)}[Nd^{3+}]_o$$

Rate = 1.8×10^{-4} [M min^{-1}]

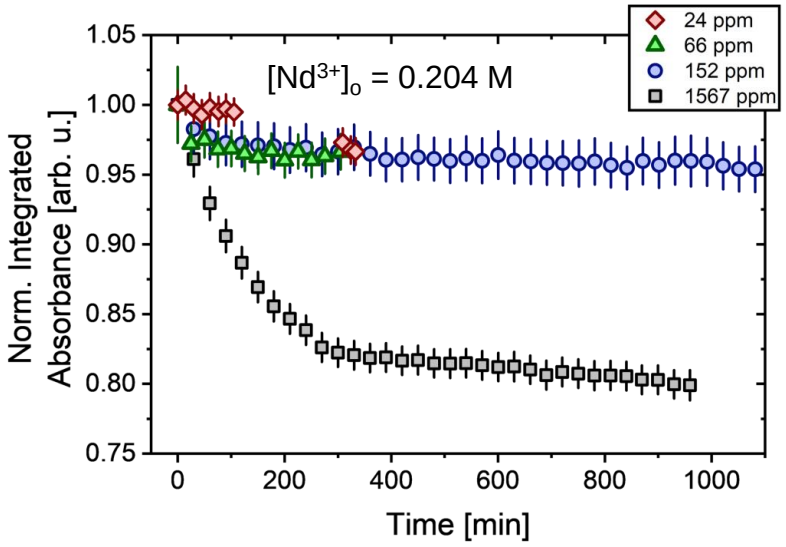
Nd consumed = 0.19 [fr.]

[Nd^{3+}] decrease is tracked for various Li_2O loadings



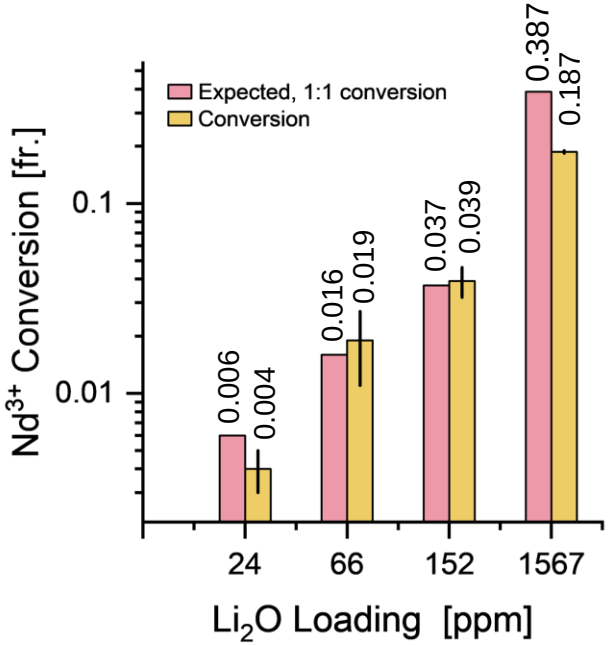


Low Li_2O loadings yield oxychloride products



Loading Li_2O [ppm]	Ratio $[O^{2-}]/[Nd^{3+}]$	Rate [M min^{-1}]	Nd Conversion [fr.]
24	0.006	$1.8 \pm 0.9 \times 10^{-5}$	0.004 ± 0.001
66	0.016	$4 \pm 1 \times 10^{-5}$	0.019 ± 0.008
152	0.037	$6.3 \pm 0.5 \times 10^{-5}$	0.039 ± 0.007
1567	0.387	$1.8 \pm 0.1 \times 10^{-4}$	0.187 ± 0.003

- Rates are similar compared to literature[3]
- **Approximate equimolar loss of Nd^{3+}**



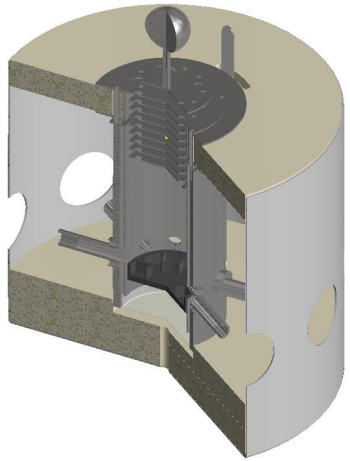
$$NdCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons NdOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

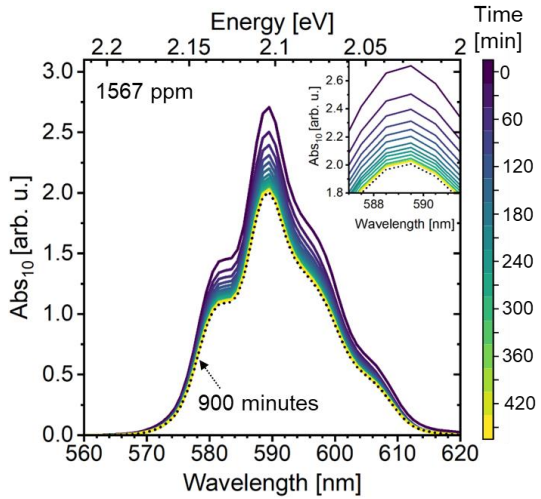
$$NdCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Nd_2O_{3(s)} \downarrow + 3LiCl_{(l)}$$

Not conclusive, but strongly suggests the formation of oxychloride products

[3] V. A. Volkovich, A. A. Ryzhov, A. B. Ivanov, A. V. Shchetinskiy, and D. S. Maltsev, Journal of The Electrochemical Society **168, 046513 (2021).**

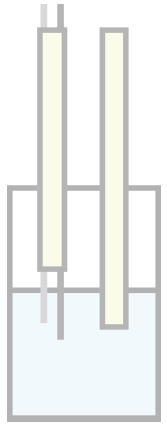
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy

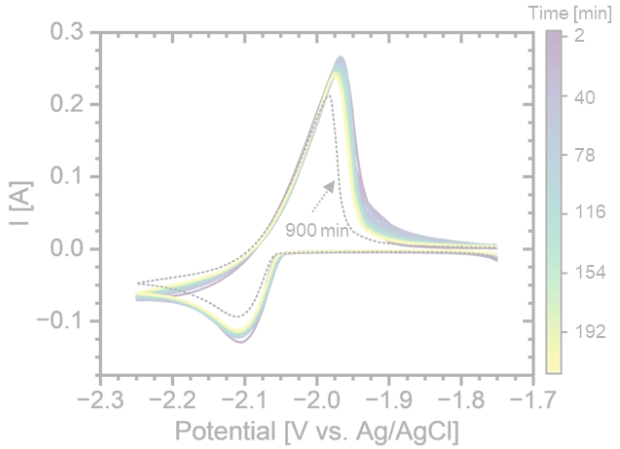




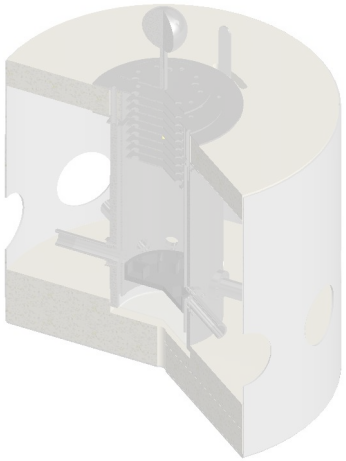
- Absorption spectroscopy works well to track Ln^{3+} concentrations in real-time
- Low loadings of O^{2-} product primarily oxychlorides

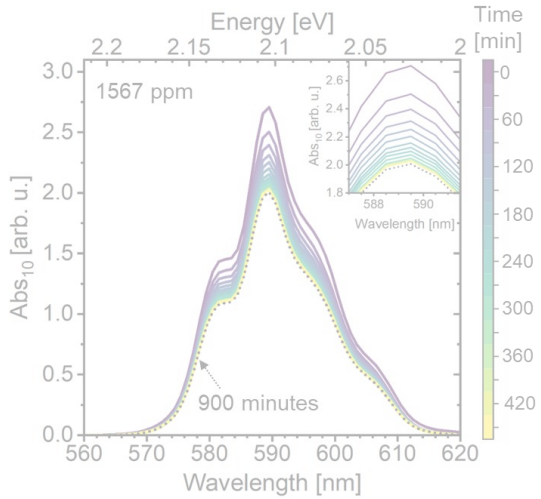
Track reaction of Pr^{3+} with O^{2-} using both absorption spectroscopy and electrochemistry





Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy





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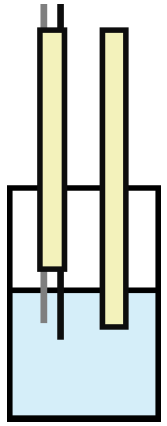
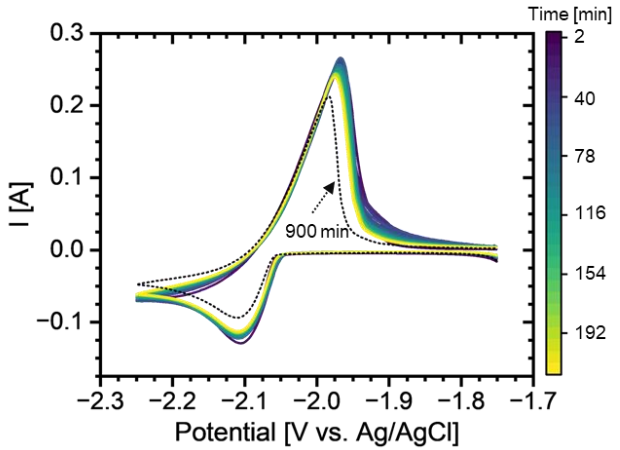
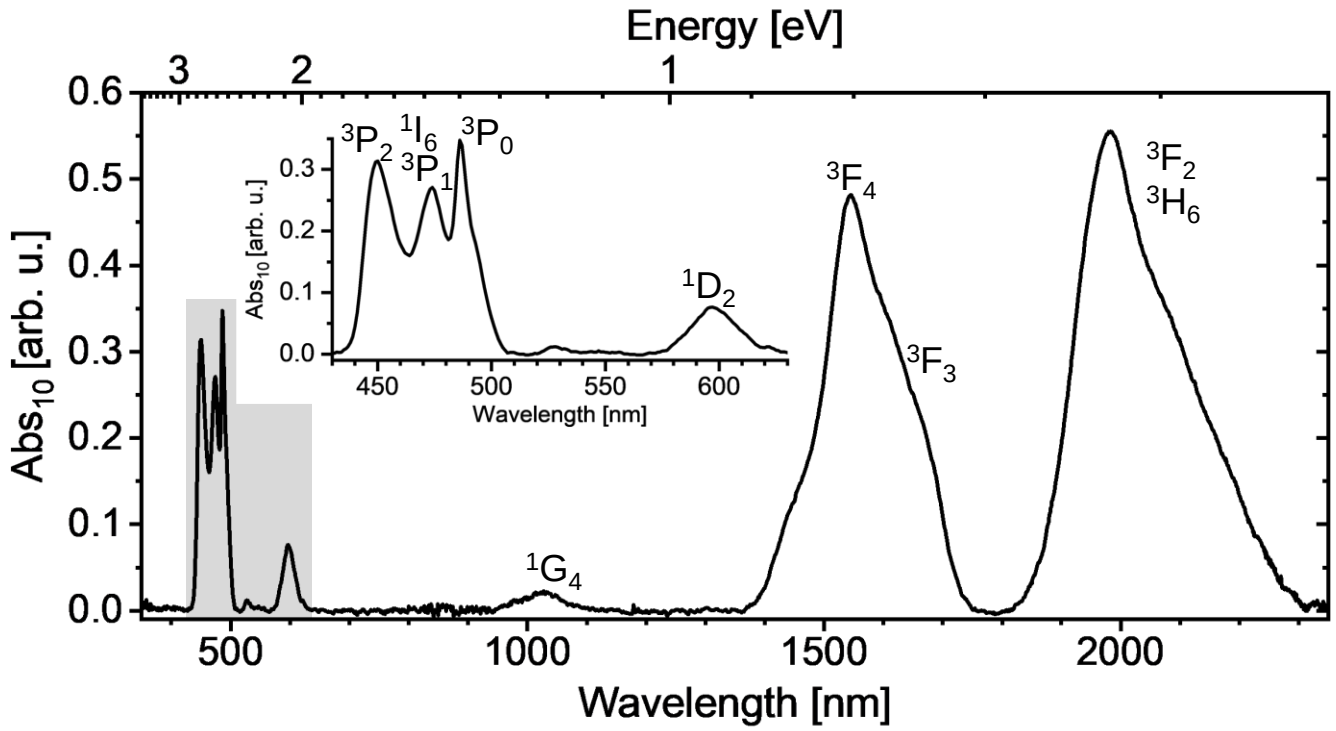




Tracking lower absorbing species: Pr^{3+}



Pr has an ~7x lower absorption coefficient than Nd

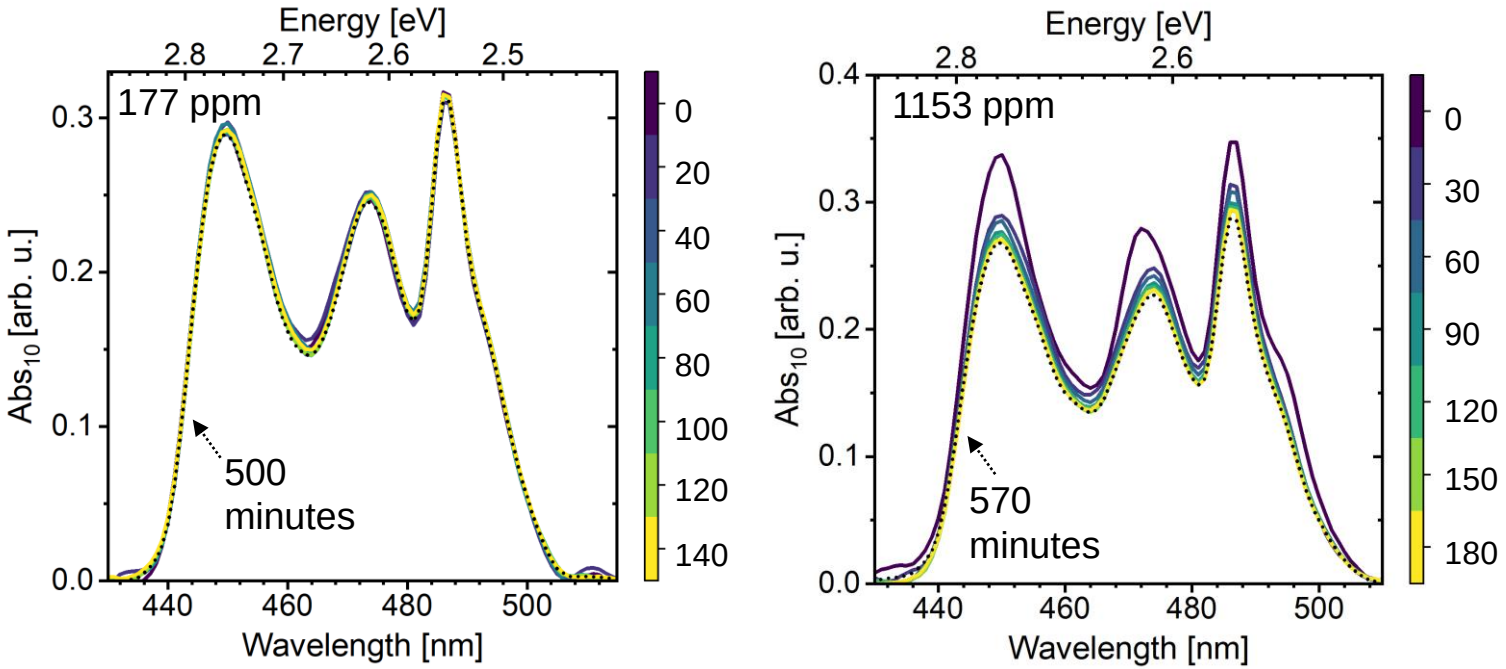
Similar reactions as Nd^{3+} with O^{2-}

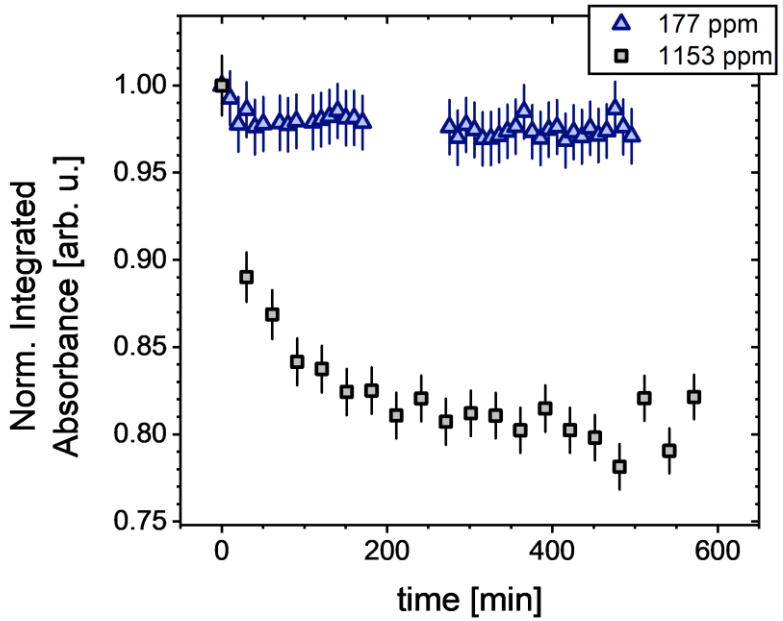
$$PrCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons PrOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

$$PrCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Pr_2O_{3(s)} \downarrow + 3LiCl_{(l)}$$

Tracking with optical spectroscopy is possible, needs to be supplemented

[Pr^{3+}] can be reasonably monitored with spectroscopy

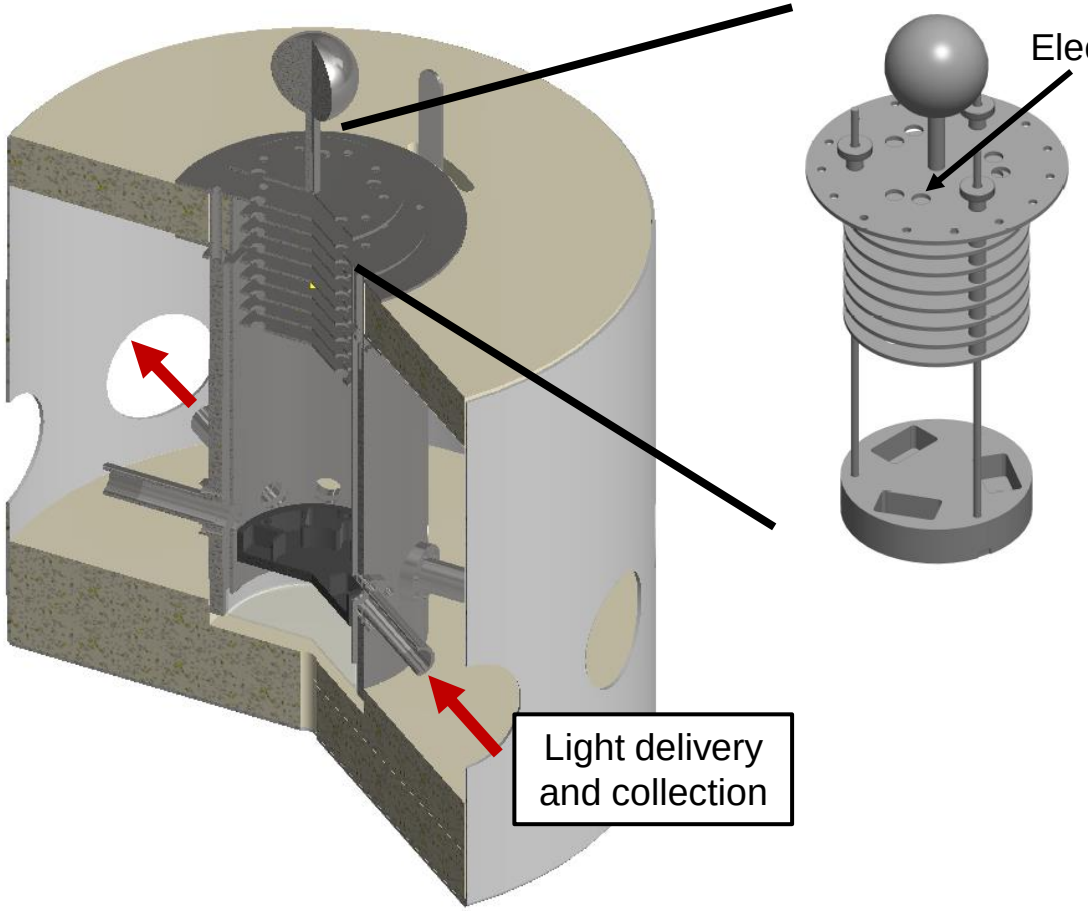




- Optical spectroscopy yields reasonable monitoring capabilities
- Can this data be supplemented with electrochemistry?

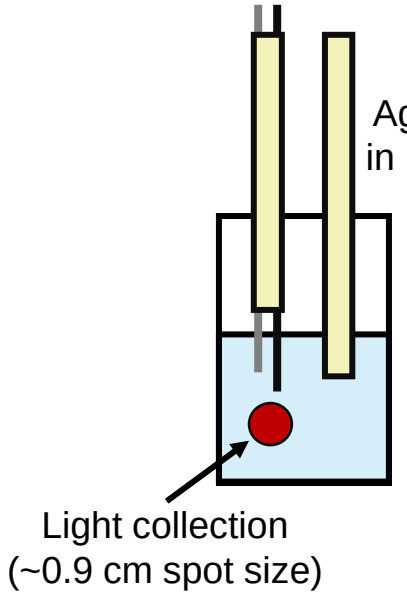
Tracking concentrations: spectroscopy *and* electrochemistry

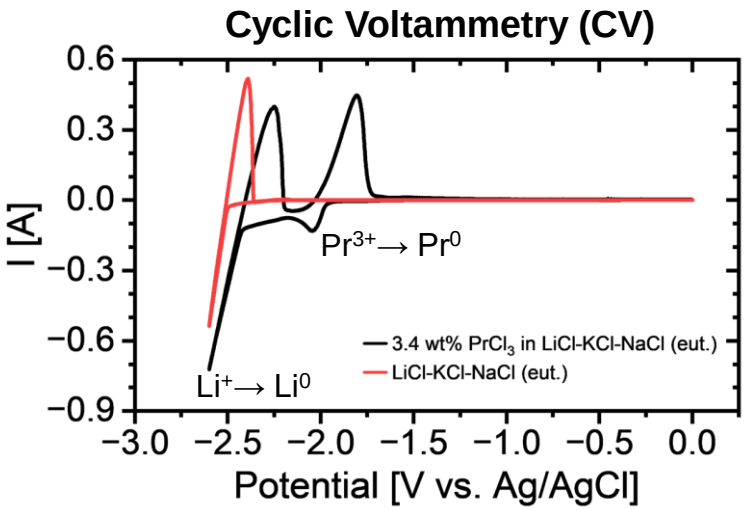
High-temperature transmission setup



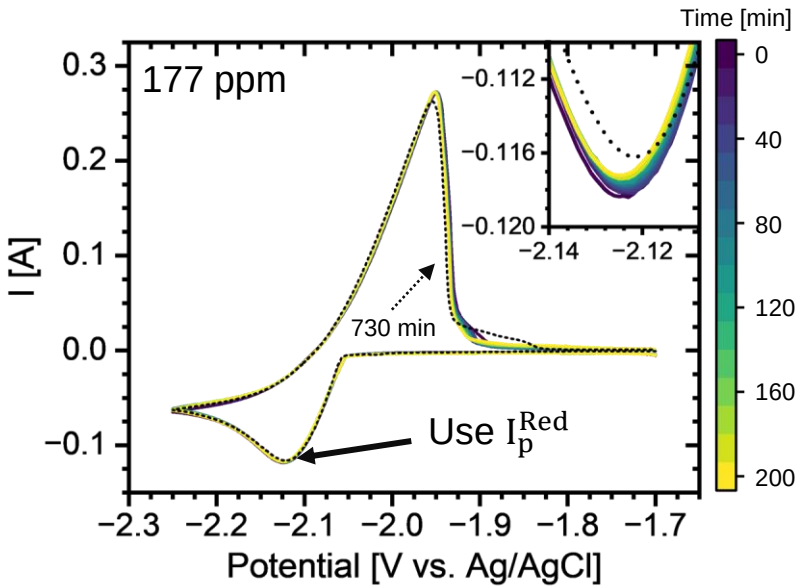
Modified rack for simultaneous measurements

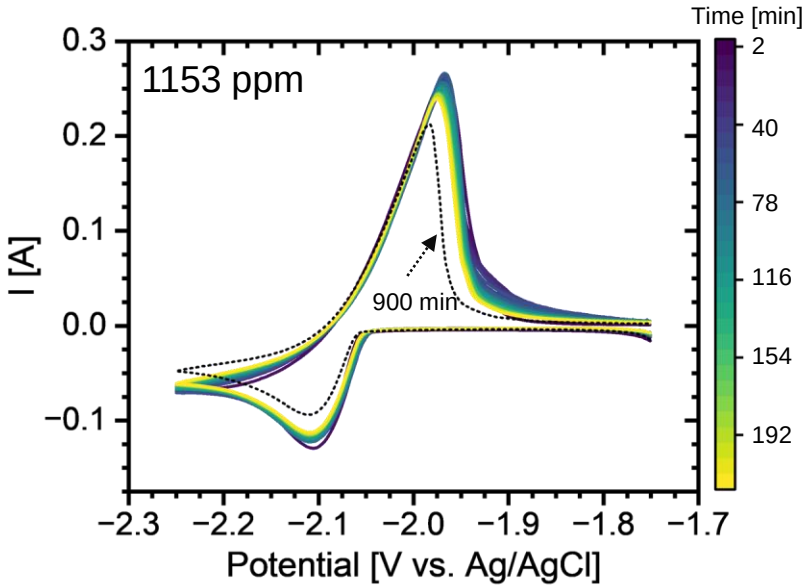
Working: Tungsten (0.5 mm wire)
Counter: Graphite (1 mm rod)

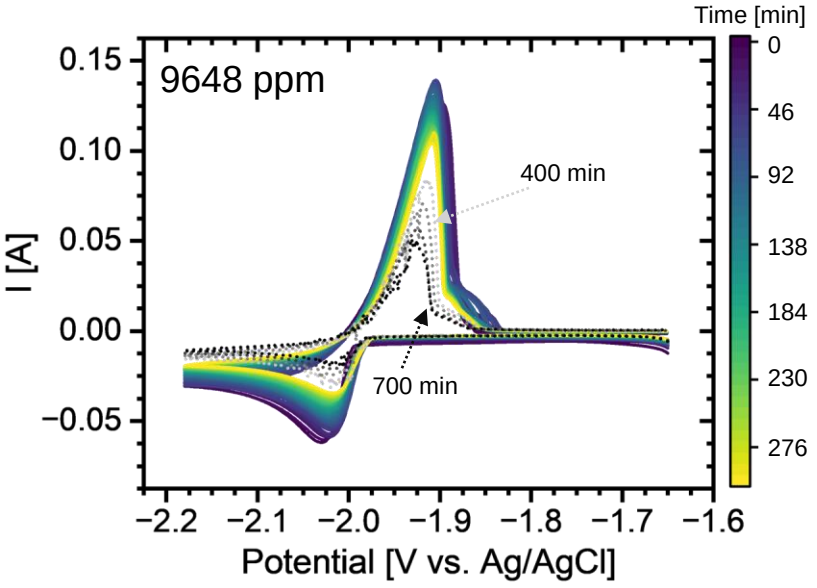




[Pr^{3+}] can also be reasonably monitored with CV

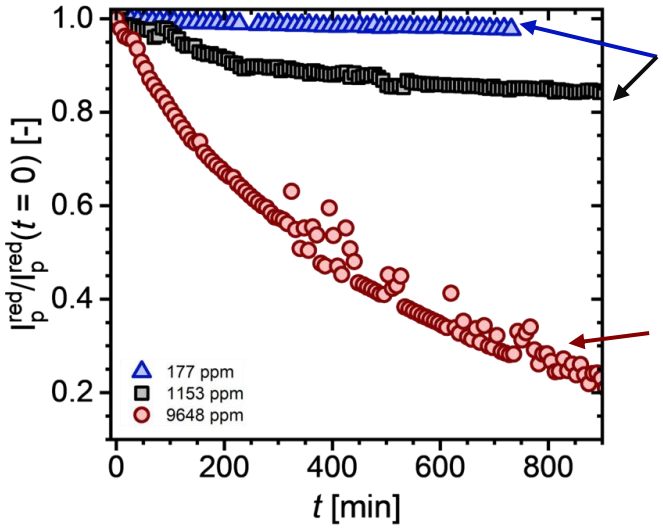






Assuming diffusion coefficient of reactant, Pr^{3+} remains similar at all Li_2O loadings

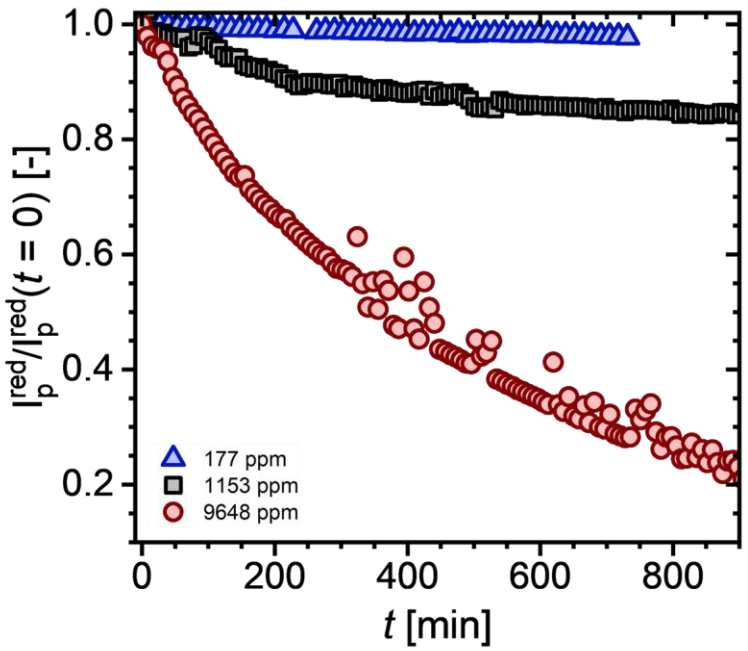
$$I_p^{Red} \propto [C]_{reactant}$$



Can be compared to optical data

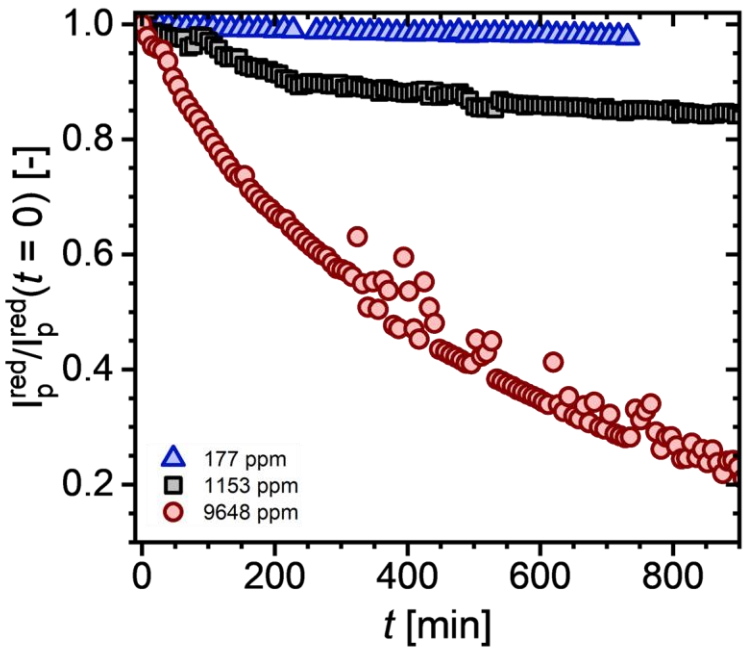
Can *not* be measured with optical spectroscopy due to turbid solution

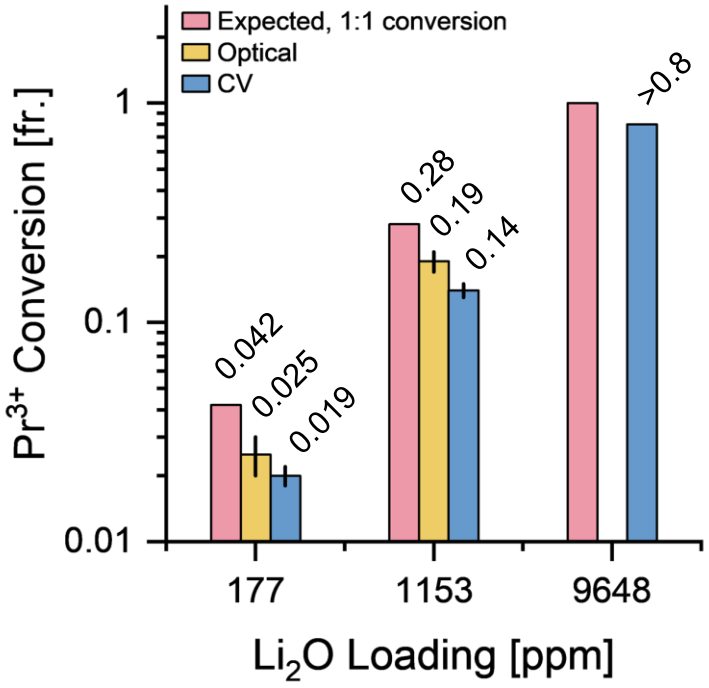
CV analysis yields rates ~3x lower than spectral analysis



Loading Li_2O [ppm]	Ratio $[O^{2-}]/[Pr^{3+}]$	Rate, Optical [M min^{-1}]	Conversion, Optical [fr.]	Rate, CV [M min^{-1}]	Conversion, CV [fr.]
177	0.042	$4.5 \pm 0.9 \times 10^{-5}$	0.025 ± 0.005	$1.46 \pm 0.07 \times 10^{-5}$	0.019 ± 0.002
1153	0.281	$2.3 \pm 0.2 \times 10^{-4}$	0.19 ± 0.02	$8.1 \pm 0.9 \times 10^{-5}$	0.14 ± 0.01
9648	2.436	--	--	$4 \pm 1 \times 10^{-4}$	> 0.8

Pr^{3+} conversion results are similar for CV and spectral analysis





Conversions are less than stoichiometric with O^{2-}

$$PrCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons PrOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

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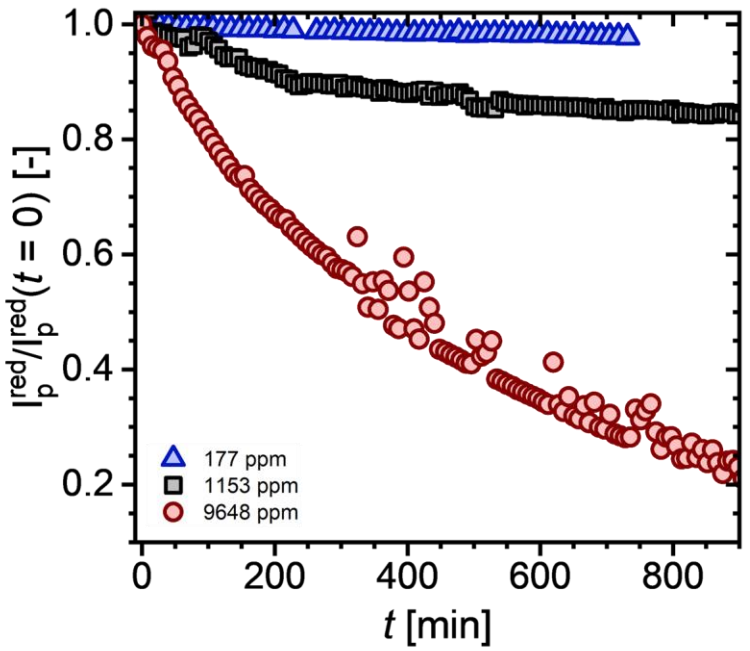
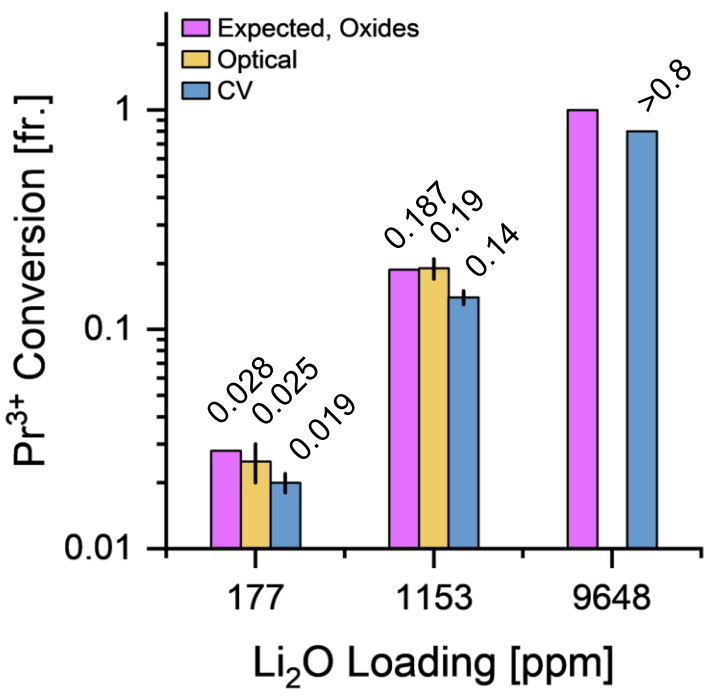
Loading Li_2O [ppm]	Ratio $[O^{2-}]/[Pr^{3+}]$	Rate, Optical [M min^{-1}]	Conversion, Optical [fr.]	Rate, CV [M min^{-1}]	Conversion, CV [fr.]
177	0.042	$4.5 \pm 0.9 \times 10^{-5}$	0.025 ± 0.005	$1.46 \pm 0.07 \times 10^{-5}$	0.019 ± 0.002
1153	0.281	$2.3 \pm 0.2 \times 10^{-4}$	0.19 ± 0.02	$8.1 \pm 0.9 \times 10^{-5}$	0.14 ± 0.01
9648	2.436	--	--	$4 \pm 1 \times 10^{-4}$	> 0.8

Pr^{3+} conversion results are similar for CV and spectral analysis





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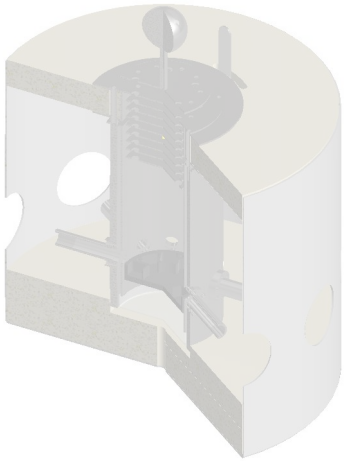
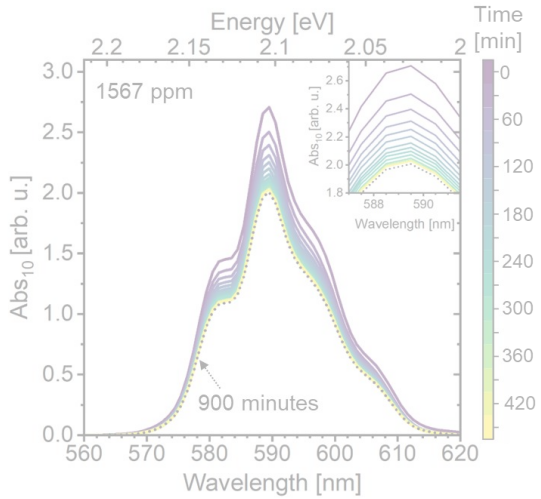
Conversion ratios match more closely with expected conversion of Pr^{3+} to predominantly oxide species

Conclusion remains tentative

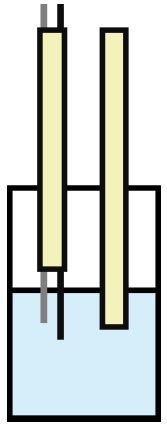
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy

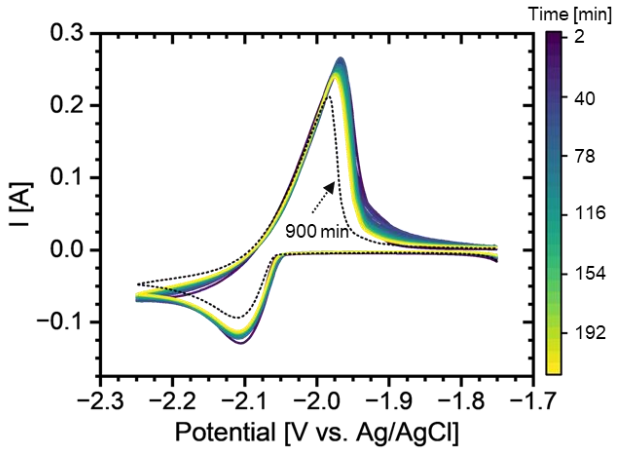




- Absorption spectroscopy works well to track Ln^{3+} concentrations in real-time
- Low loadings of O^{2-} product primarily oxychlorides

Track reaction of Pr^{3+} with O^{2-} using both absorption spectroscopy and electrochemistry





- Spectroscopy and electrochemistry provide complementary methods of analyte monitoring
  - Techniques point to similar conclusions
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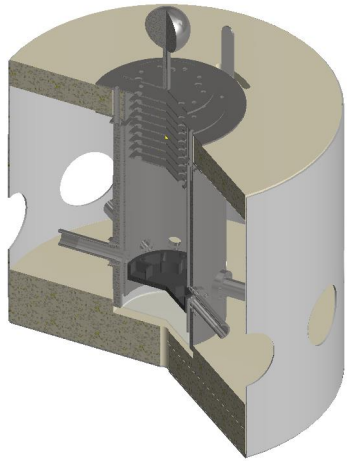

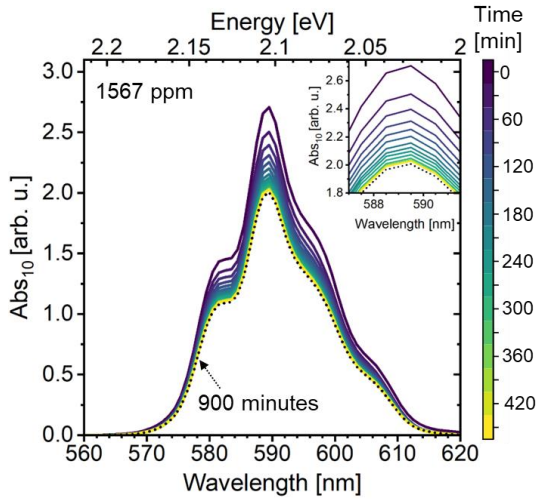

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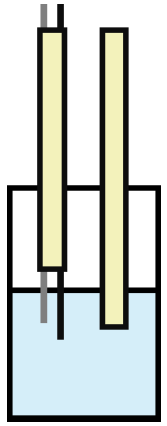

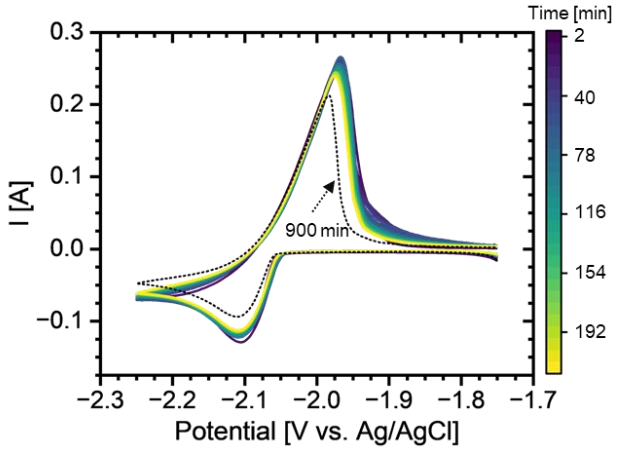

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Future work is focused on more direct structural probing of precipitates in melt

Thank you!

Idaho National Laboratory

Battelle Energy Alliance manages INL for the U.S. Department of Energy's Office of Nuclear Energy. INL is the nation's center for nuclear energy research and development, and also performs research in each of DOE's strategic goal areas: energy, national security, science and the environment.