INL/CON-24-82542-Revision-1

In situ monitoring of lanthanide reactions with oxide species via combined absorption spectroscopy and electrochemical methods

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Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

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

March 27, 2025

MARC XIII Conference

Kailua-Kona, Hawaii, United States

Garrett LeCroy
Qiufeng Yang
Guoping Cao
Ruchi Gakhar

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

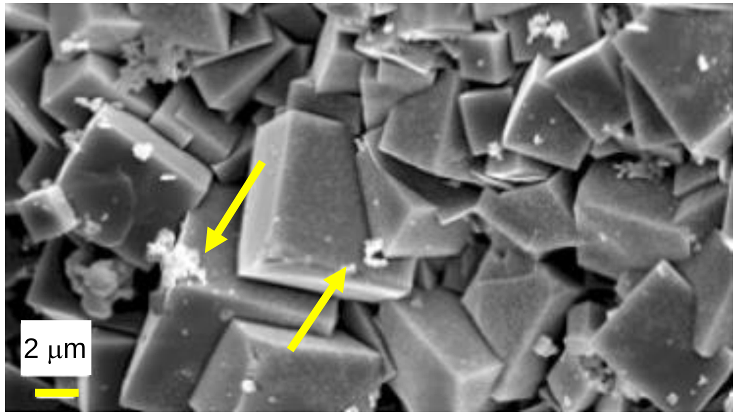
- Ln generally thought to form oxychlorides
- Temperature and lanthanide dependent[1,2]

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

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

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]

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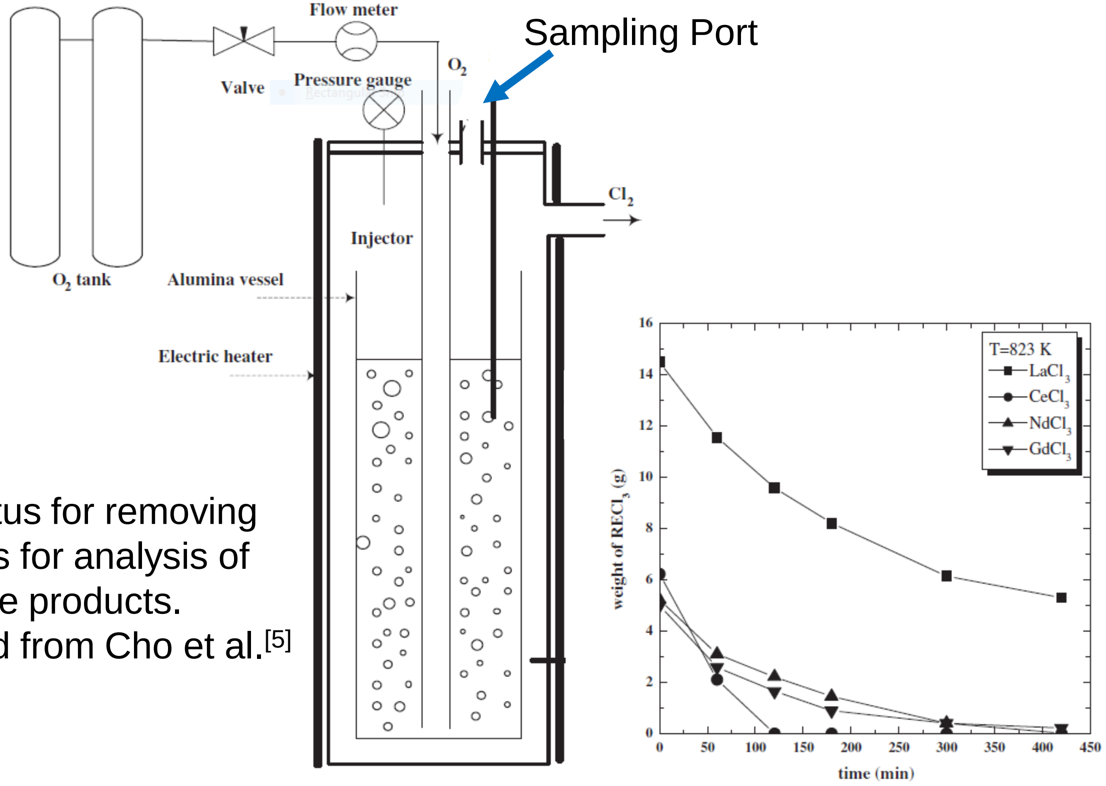
[1] Y. Katayama, et al., Journal of The Electrochemical Society **142, 2174 (1995).**
[2] Y.-Z. Cho, et al., Journal of Nuclear Materials **384, 256 (2009).**
[3] H. C. Eun, et al., Journal of Nuclear Materials **408, 110 (2011).**
[4] V. A. Volkovich, et al., Journal of The Electrochemical Society **168,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

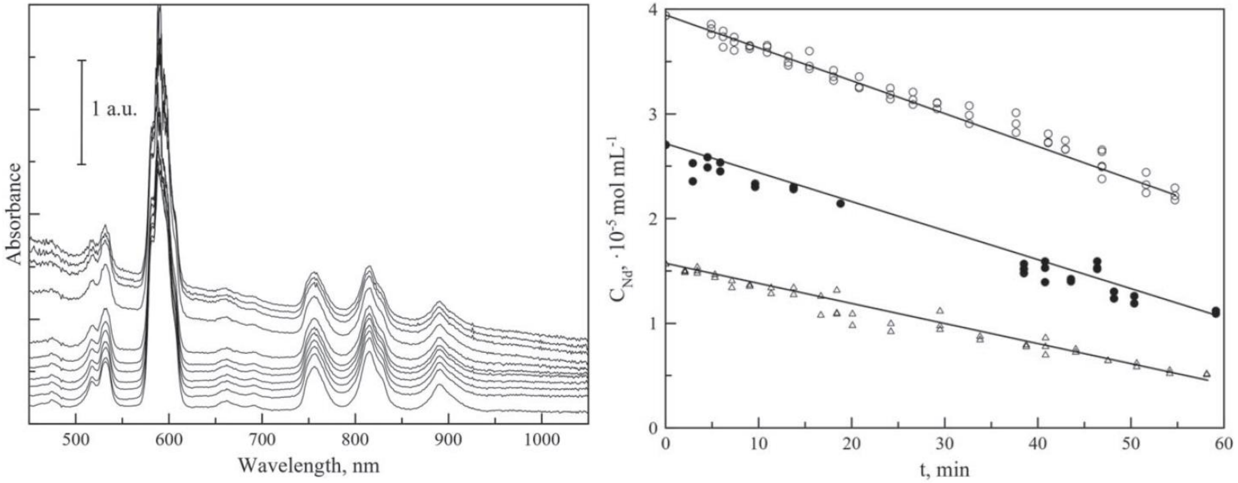
Online sampling and absorption spectroscopy have been used to track reaction kinetics/conversions

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]

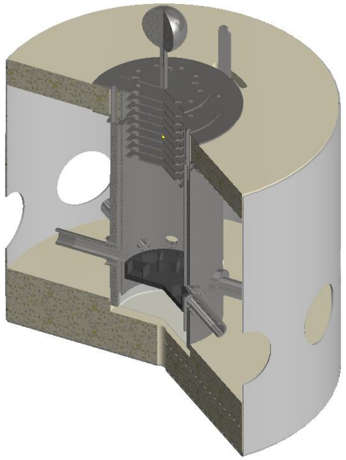


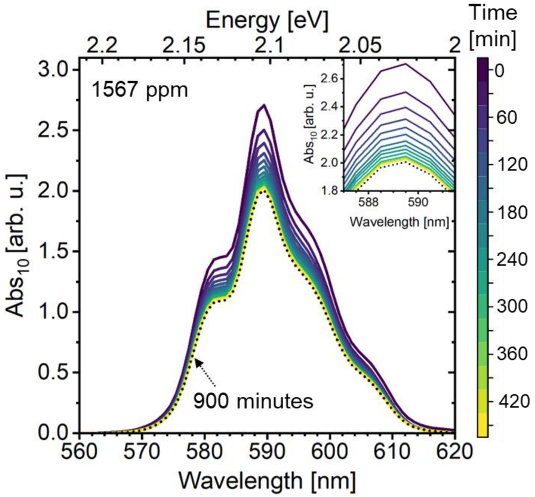
Absorption spectra of the reaction of Nd^{3+} with sparged O_2(g) and concentration of Nd^{3+} with time. Adapted from Volkovich et al.[4]

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

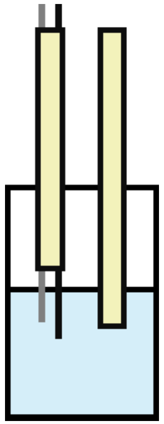
[5] .Y-J. Cho, et al., Journal of Nuclear Science and Technology **43, 1280 (2006).**

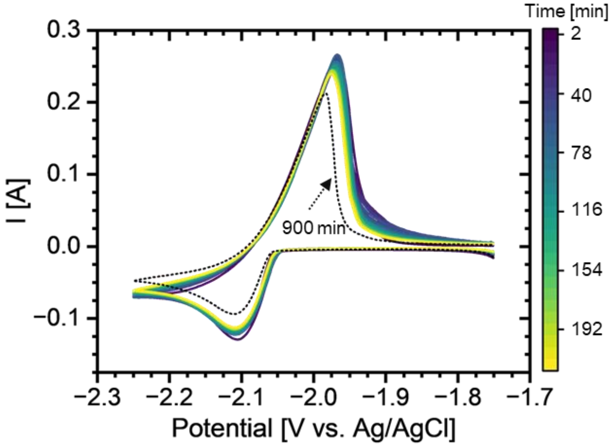
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy





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

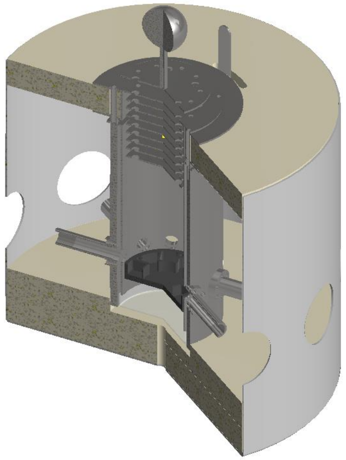


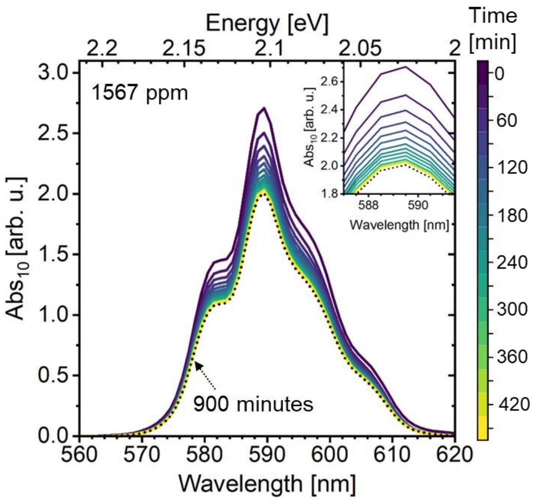


Techniques provide real-time clues

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

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





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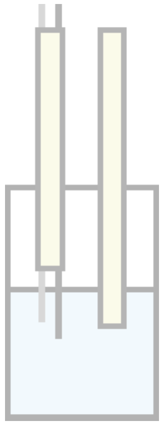
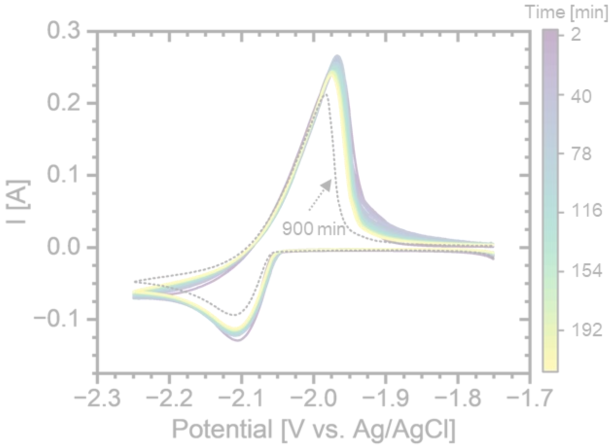
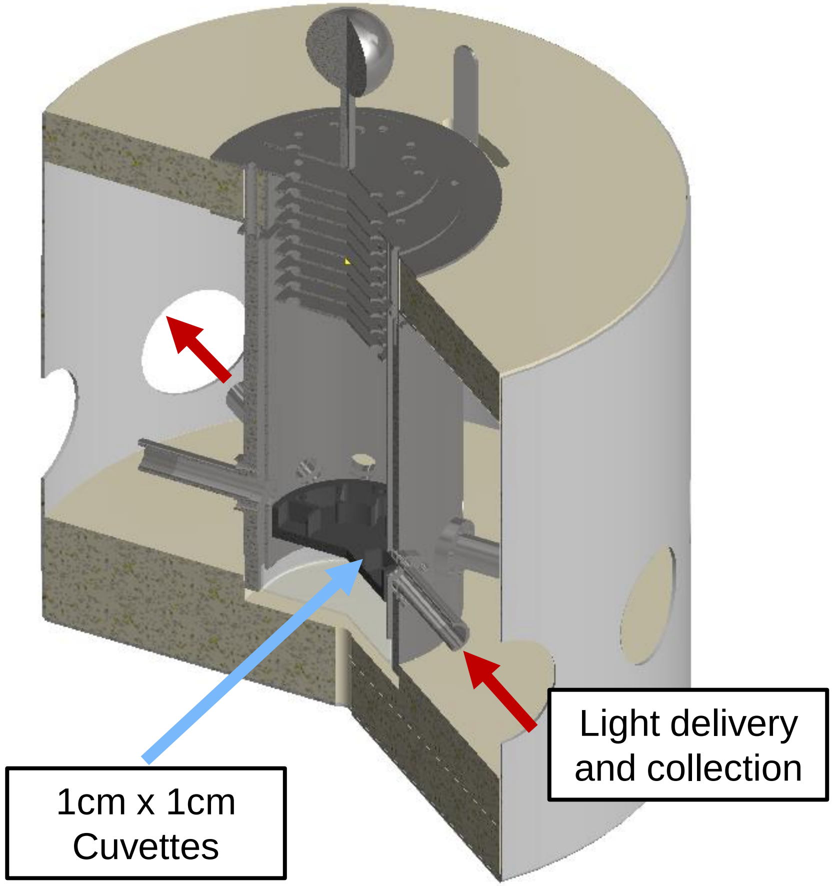




Tracking concentrations: spectroscopy

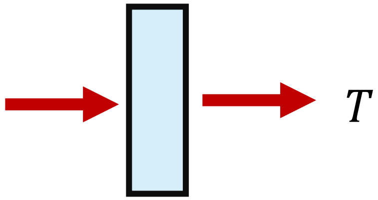
High-temperature transmission setup



1cm x 1cm Cuvettes

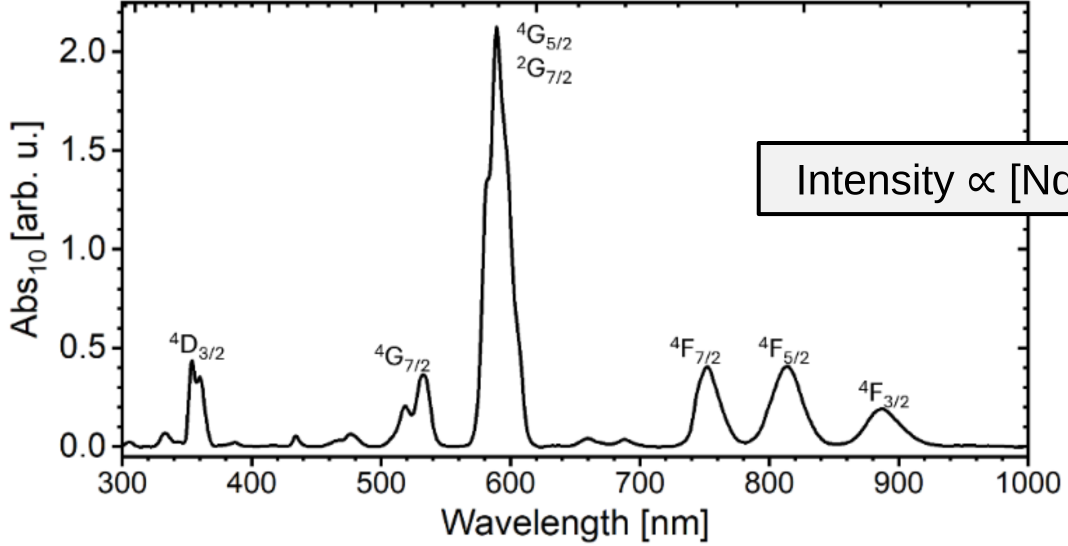
Light delivery and collection

Transmission allows concentration monitoring



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

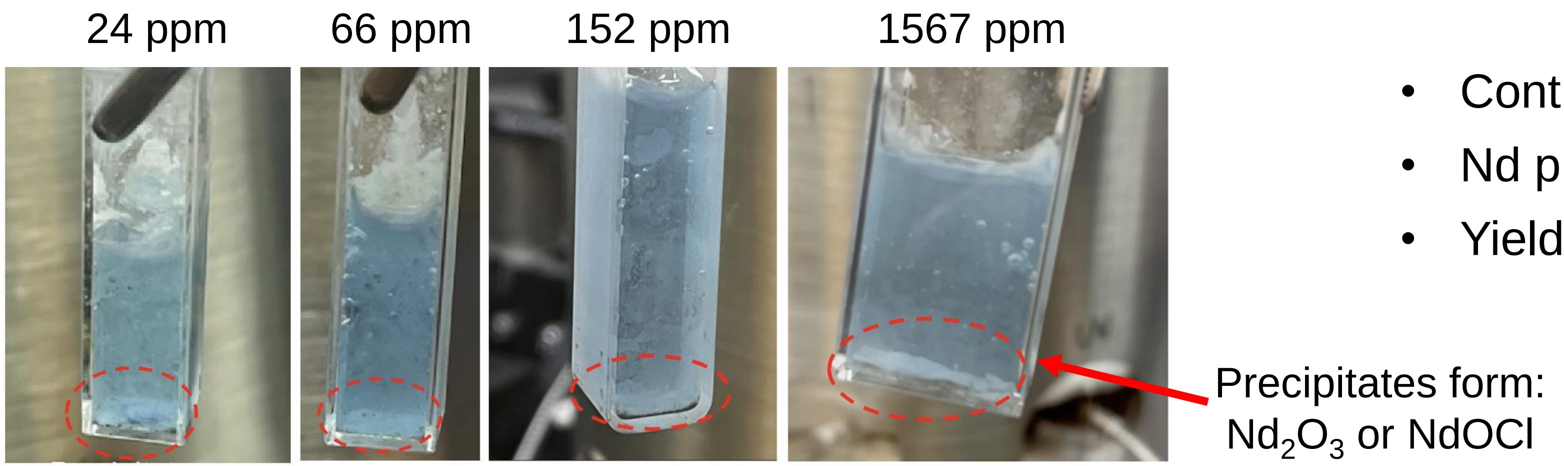
Nd^{3+} in LiCl-NaCl-KCl eutectic (500^{o}C)



Intensity ∝ [Nd^{3+}]

Oxide or oxychloride precipitates form after Li_2O addition

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



Precipitates form:
Nd_2O_3 or NdOCl

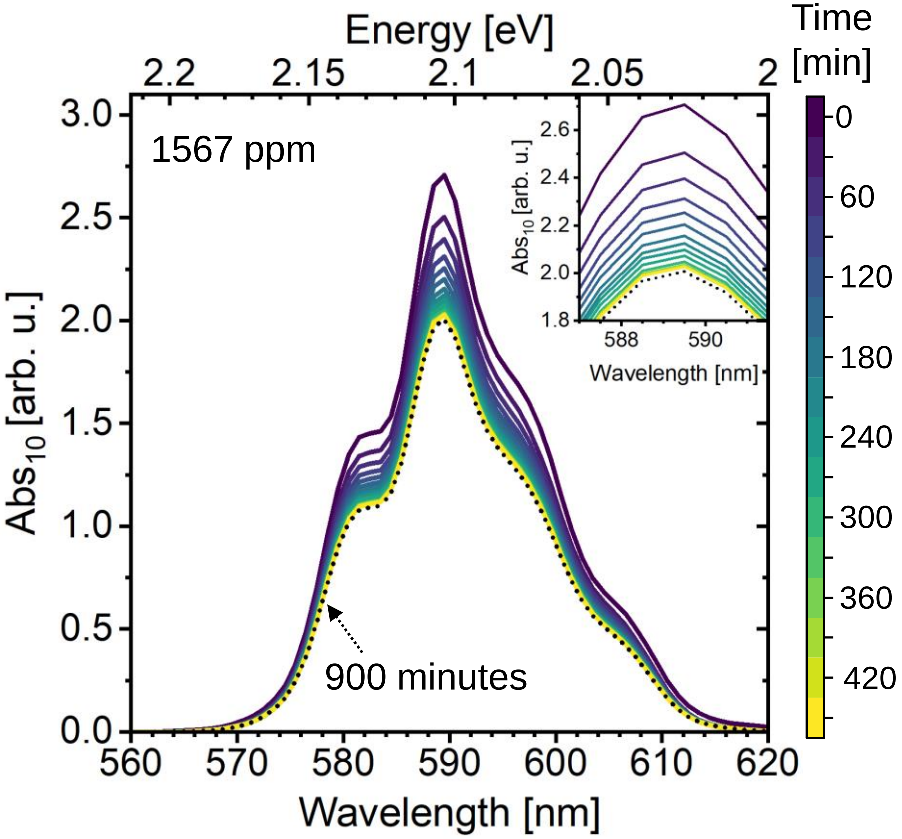
$$NdCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons \underline{NdOCl_{(s)}\downarrow} + 2LiCl_{(l)}$$

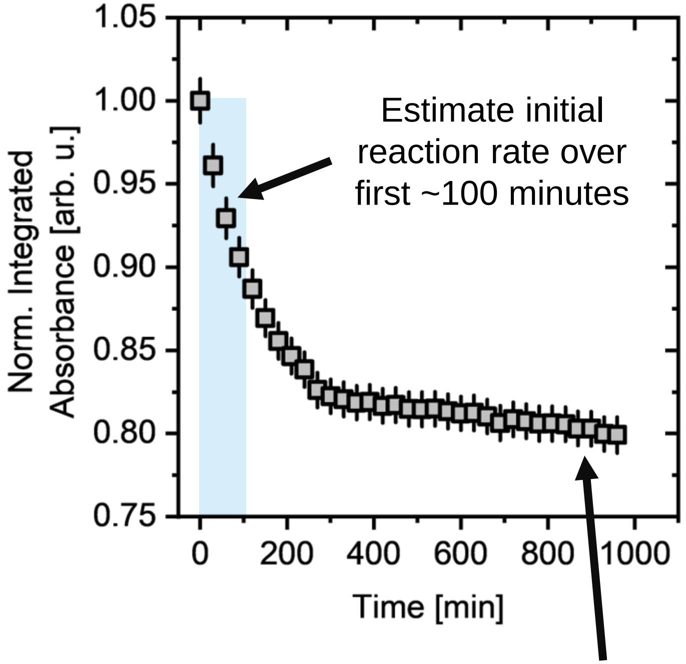
$$NdCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons \underline{0.5Nd_2O_{3(s)}}\downarrow + 3LiCl_{(l)}$$

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

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

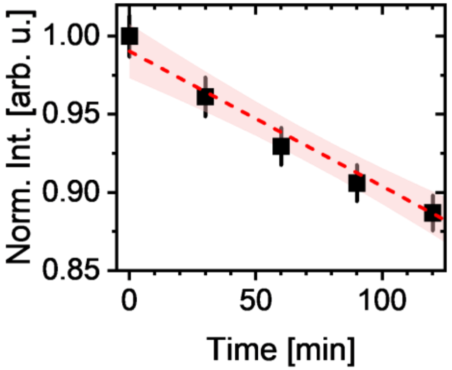
[Nd^{3+}] decreases with time after adding Li_2O: What information does absorption spectroscopy yield?





Estimate initial reaction rate over first ~100 minutes

Estimate fraction of Nd^{3+} consumed

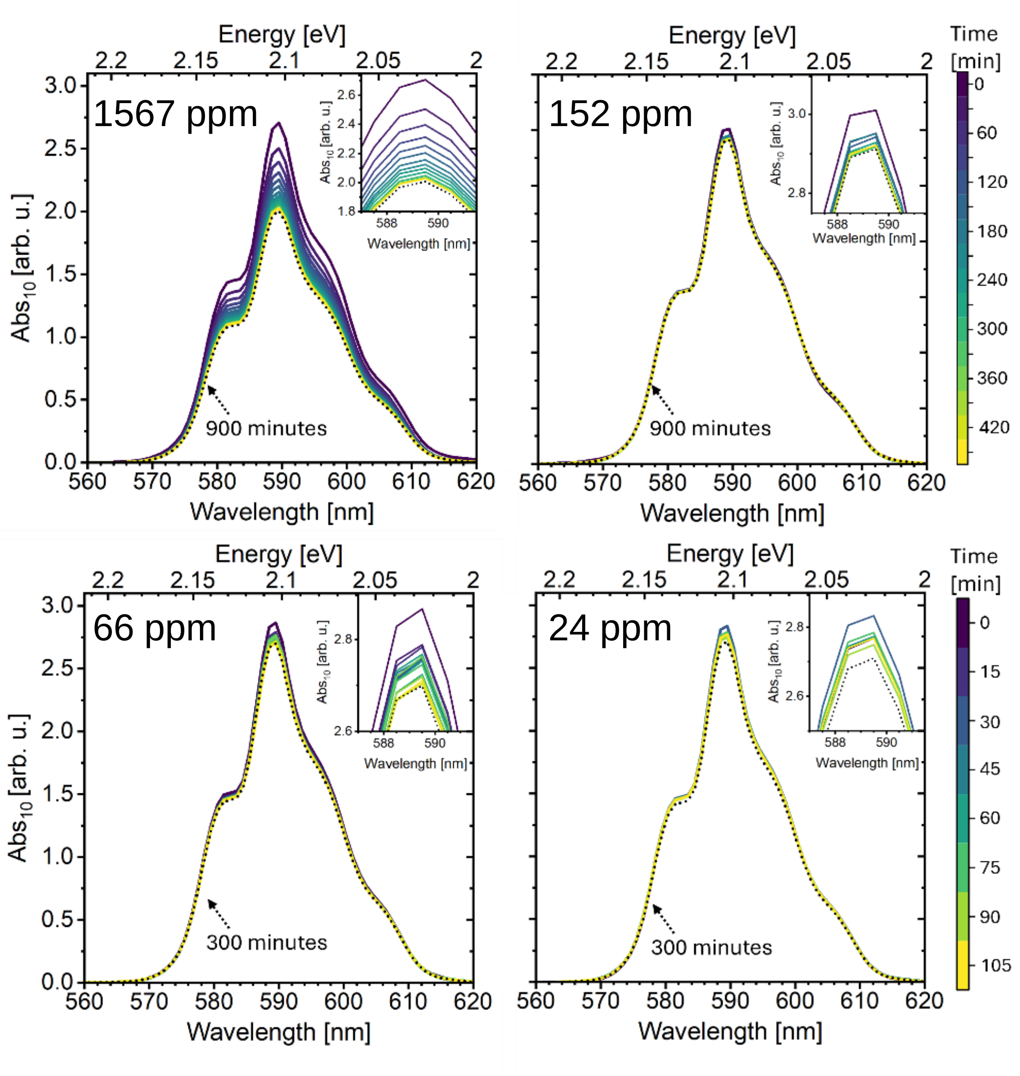


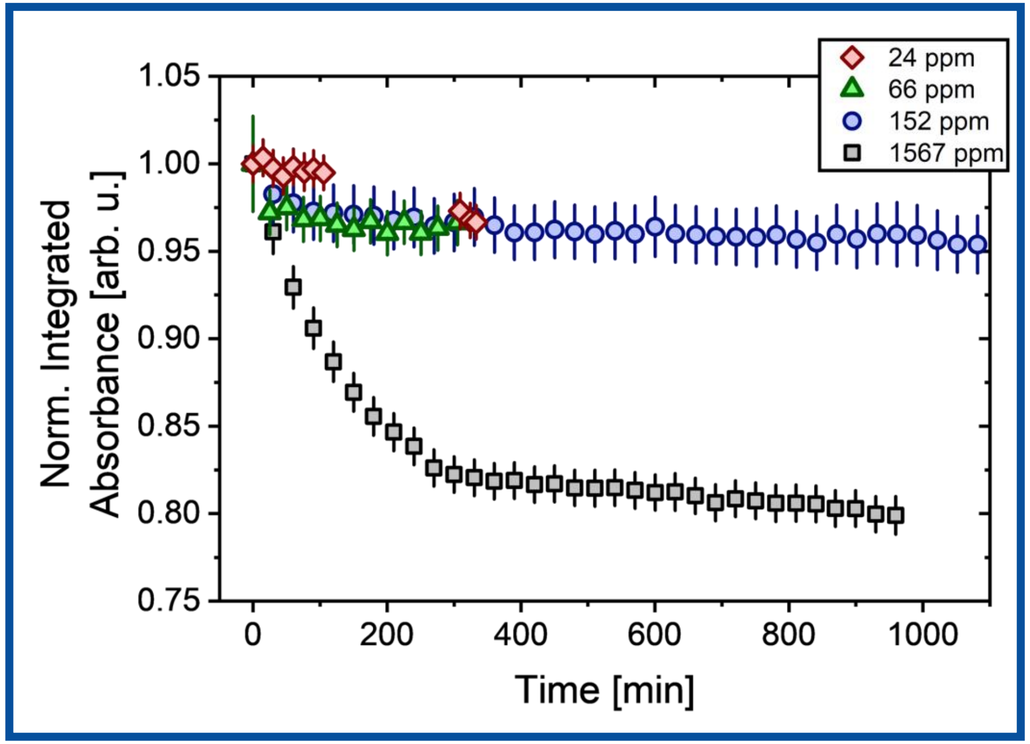
$$[Nd^{3+}](t) = \frac{\mathrm{Abs_{max}}(t)}{\mathrm{Abs_{max}}(0)} [\mathrm{Nd}^{3+}]_o$$

Rate = 1.8×10^{-4} [M min^{-1}]

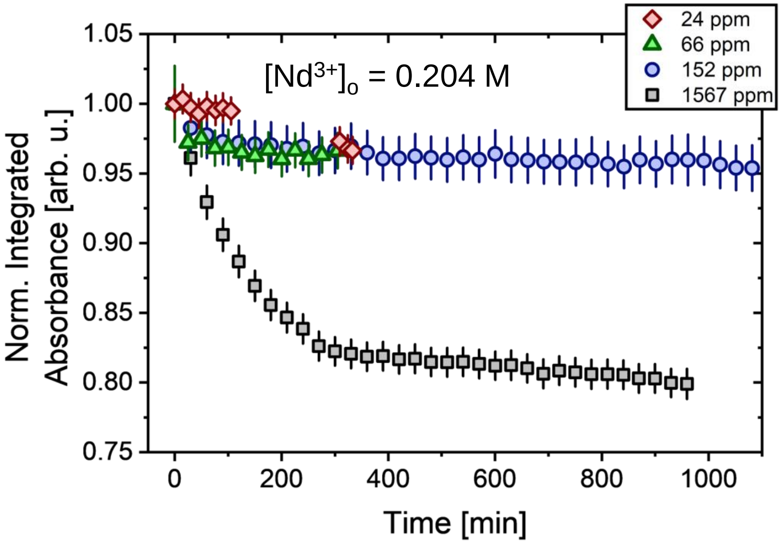
Nd consumed = 0.19 [fr.]

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



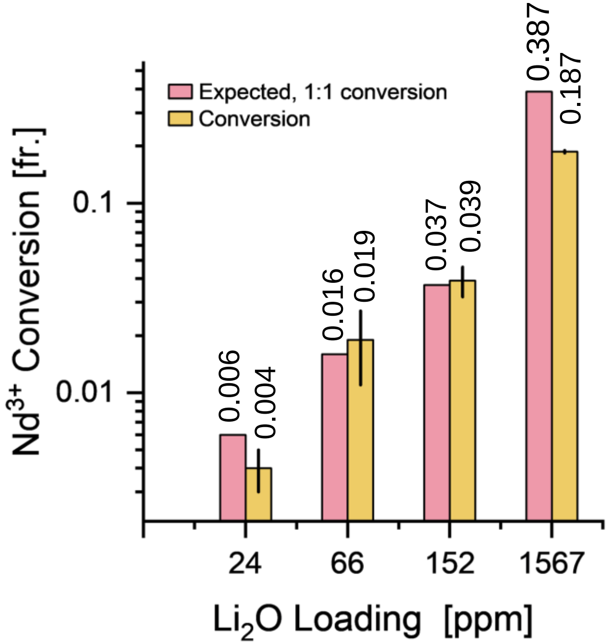


Low Li_2O loadings yield oxychloride products



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+}**



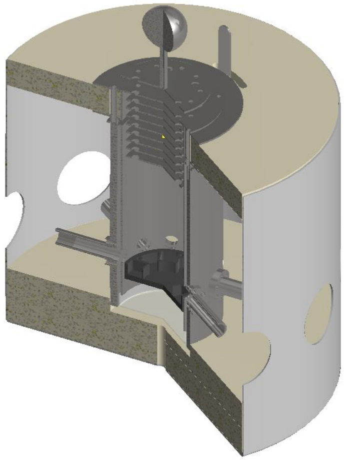
$$\boxed{NdCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons NdOCl_{(s)}\downarrow + 2LiCl_{(l)}}$$

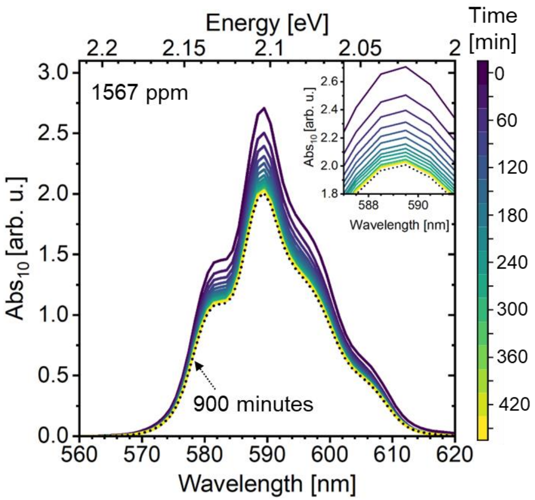
$$NdCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Nd_2O_{3(s)}\downarrow + 3LiCl_{(l)}$$

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).**

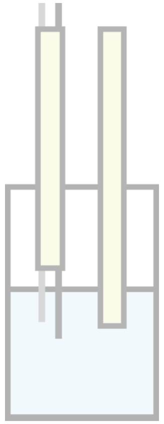
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy

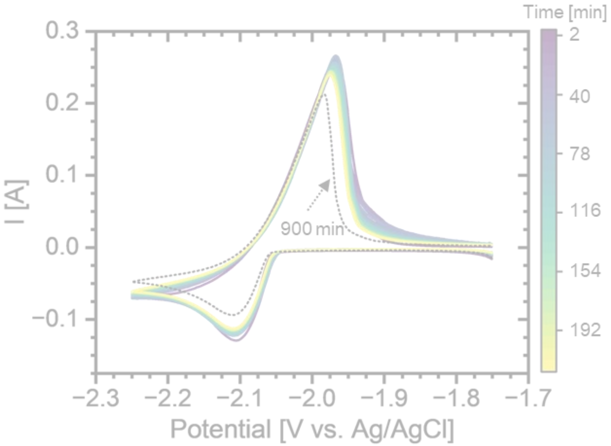




- Absorption spectroscopy works well to track Ln^{3+} concentrations in real-time
- Low loadings of O^{2-} product primarily oxychlorides

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





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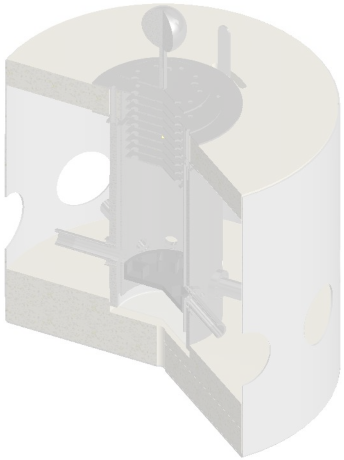

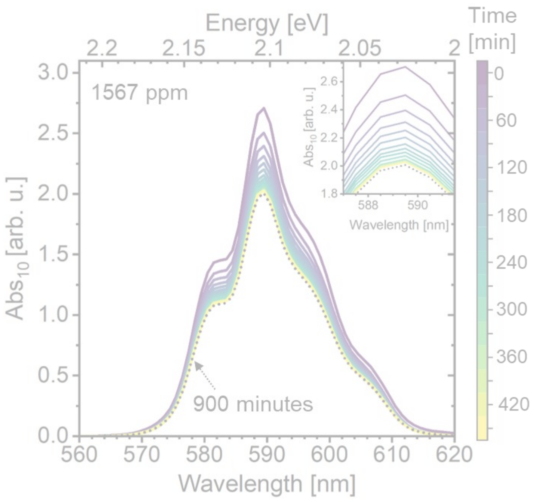

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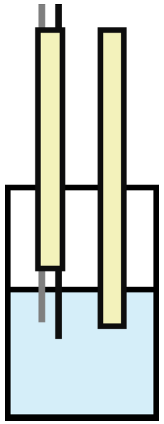
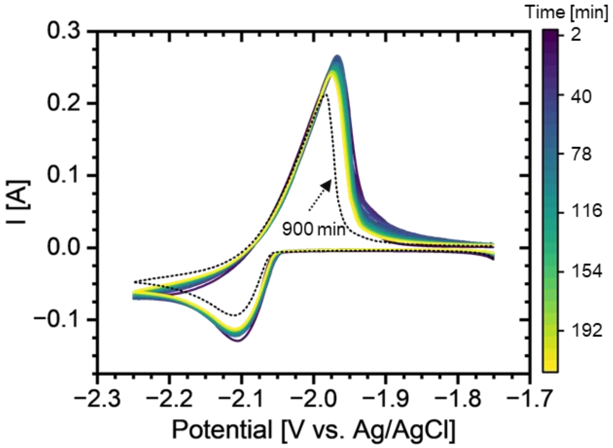
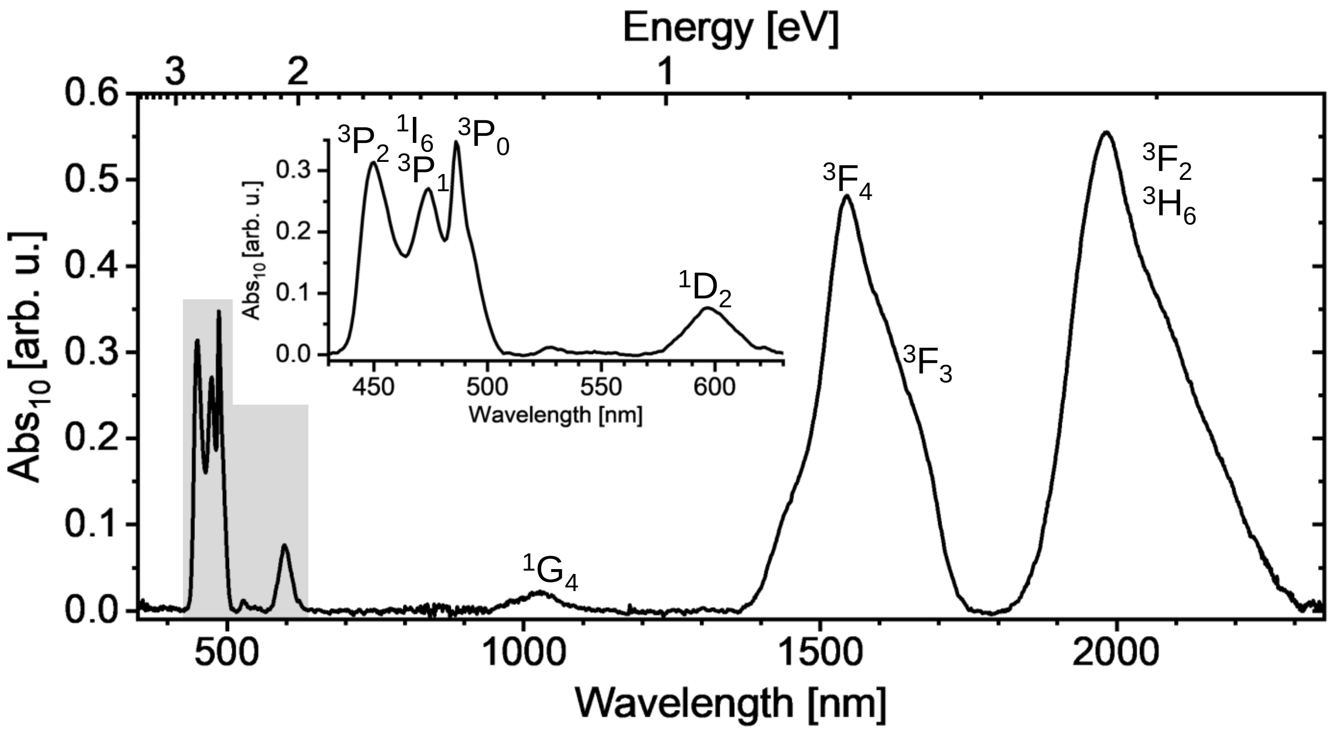




Tracking lower absorbing species: Pr^{3+}



Pr has an ~7x lower absorption coefficient than Nd

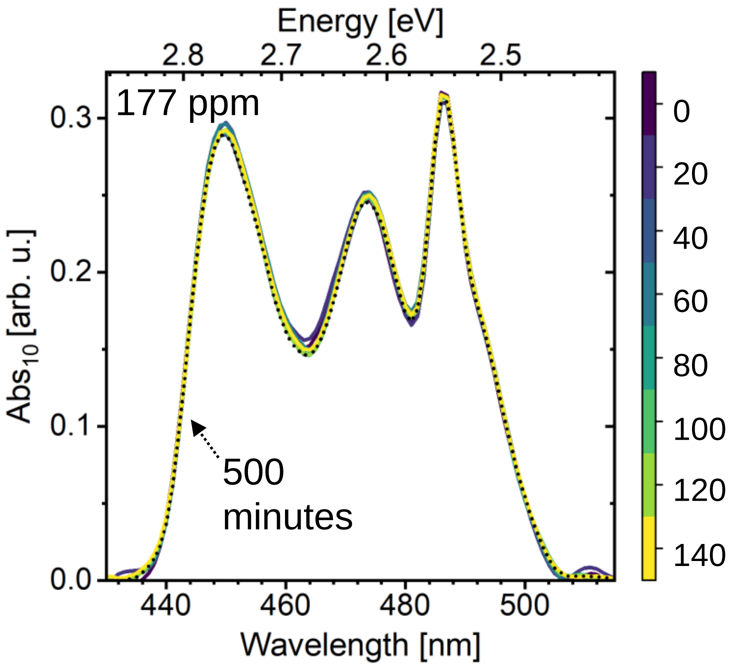
Similar reactions as Nd^{3+} with O^{2-}

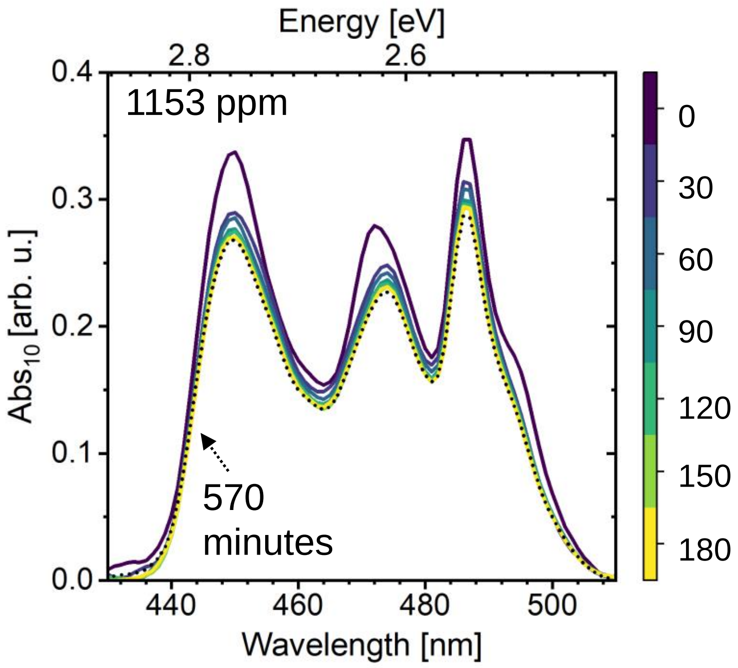
$$PrCl_{3(l)} + Li_2O_{(l)} \leftrightharpoons PrOCl_{(s)} \downarrow + 2LiCl_{(l)}$$

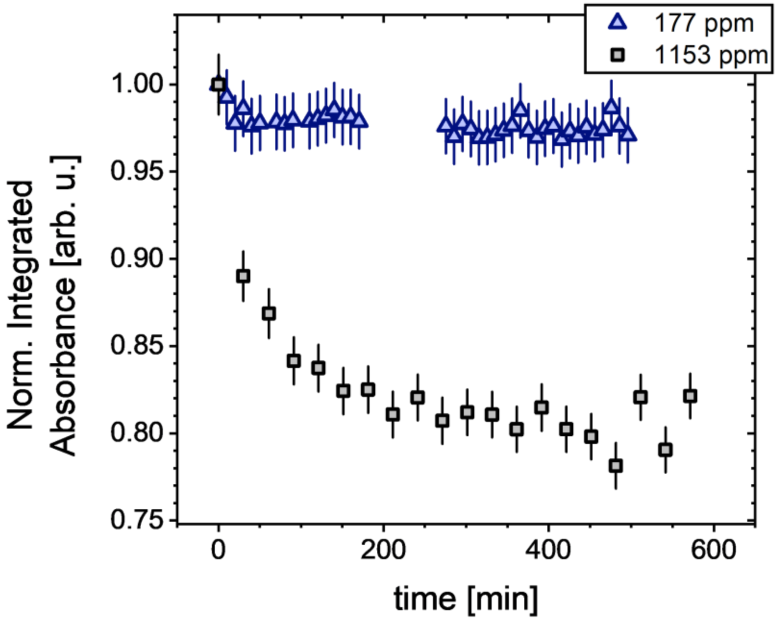
$$PrCl_{3(l)} + 1.5Li_2O_{(l)} \leftrightharpoons 0.5Pr_2O_{3(s)} \downarrow + 3LiCl_{(l)}$$

Tracking with optical spectroscopy is possible, needs to be supplemented

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



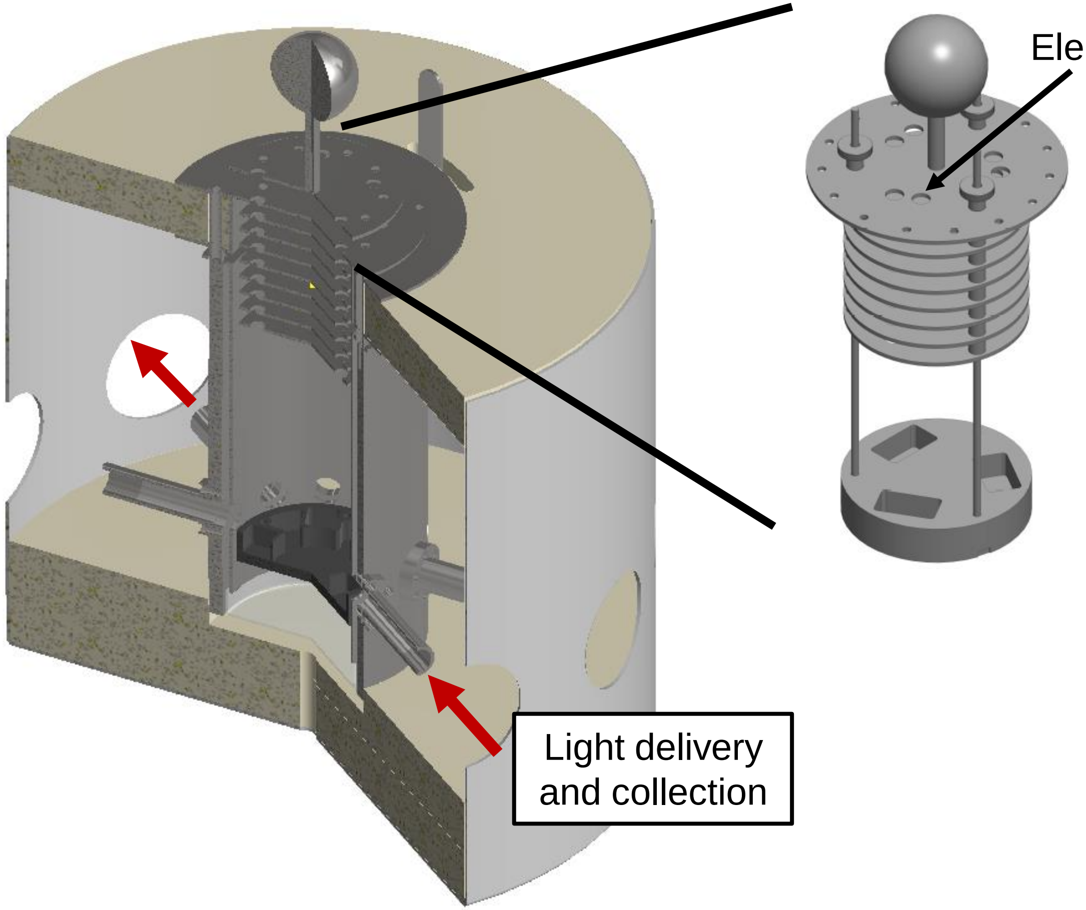




- Optical spectroscopy yields reasonable monitoring capabilities
- Can this data be supplemented with electrochemistry?

Tracking concentrations: spectroscopy *and* electrochemistry

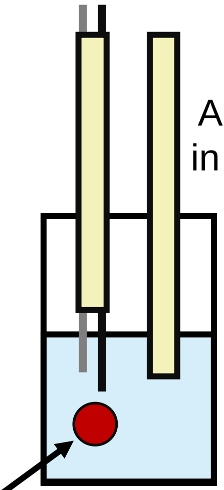
High-temperature transmission setup



Modified rack for simultaneous measurements

Electrodes

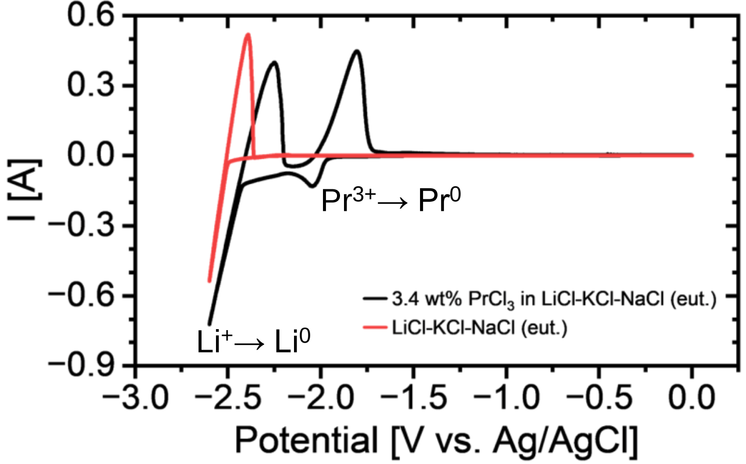
Working: Tungsten (0.5 mm wire)
Counter: Graphite (1 mm rod)



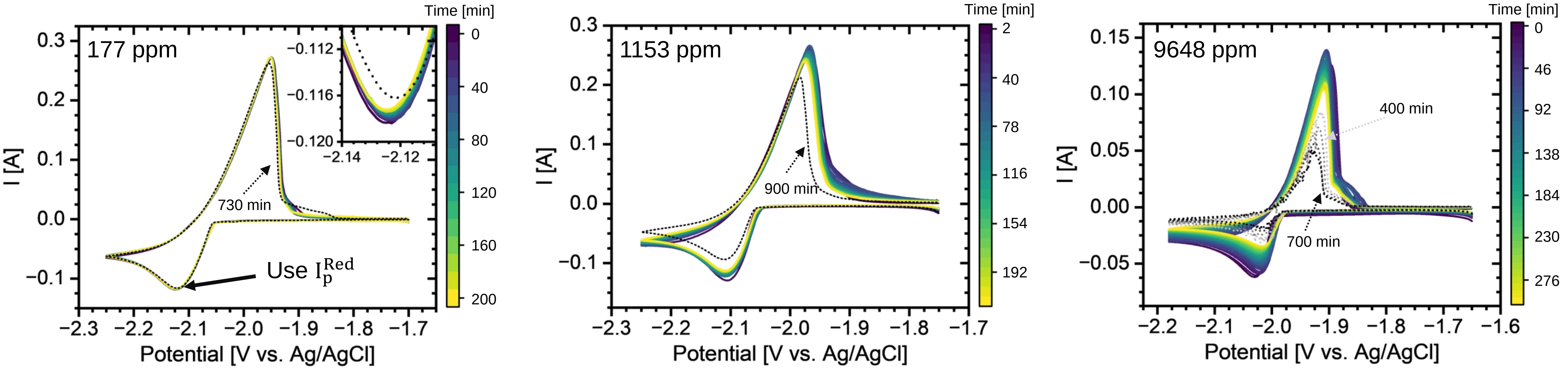
Ag/AgCl Ref.
in mullite tube

Light collection
(~0.9 cm spot size)

Cyclic Voltammetry (CV)

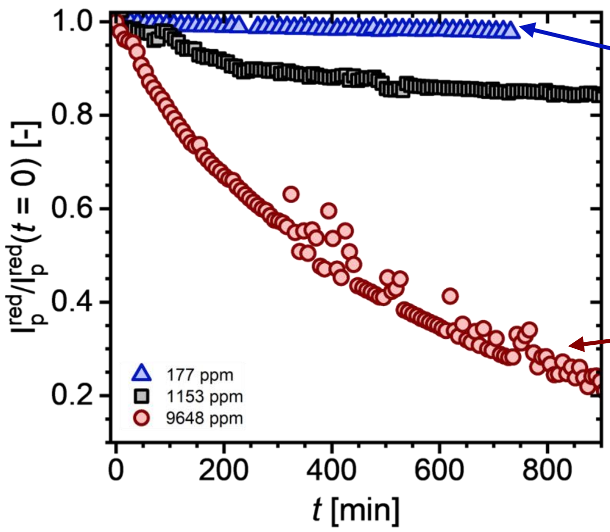


$[Pr^{3+}]$ can also be reasonably monitored with CV



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

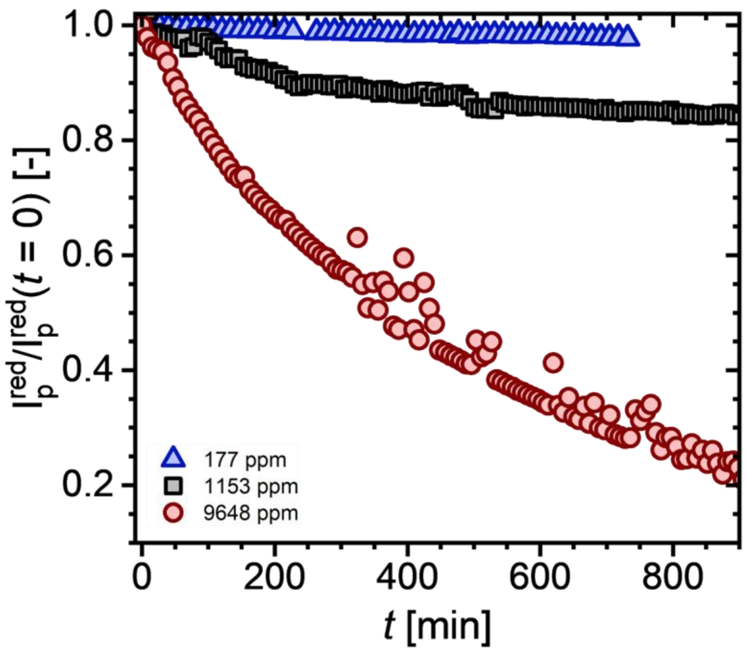
$$\boxed{I_p^{Red} \propto [C]_{reactant}}$$



Can be compared to optical data

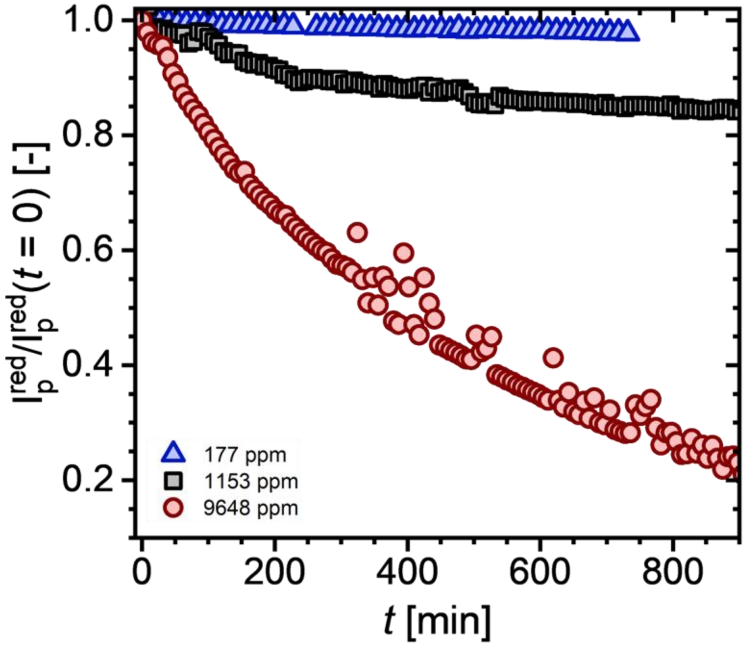
Can *not* be measured with optical spectroscopy due to turbid solution

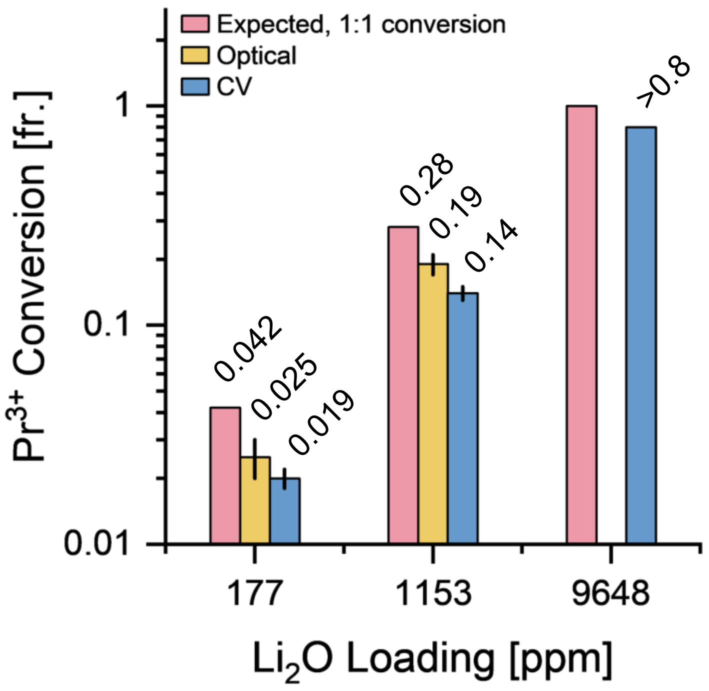
CV analysis yields rates ~3x lower than spectral analysis



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





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

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

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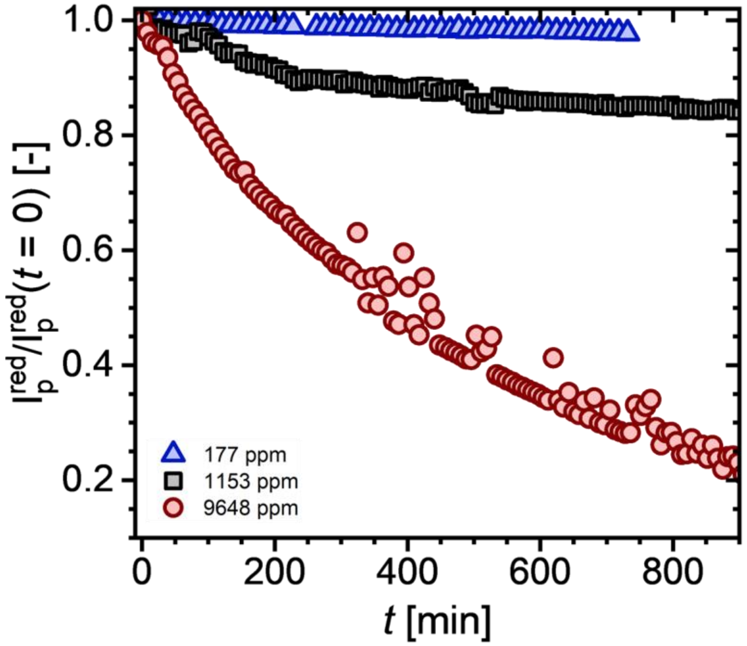

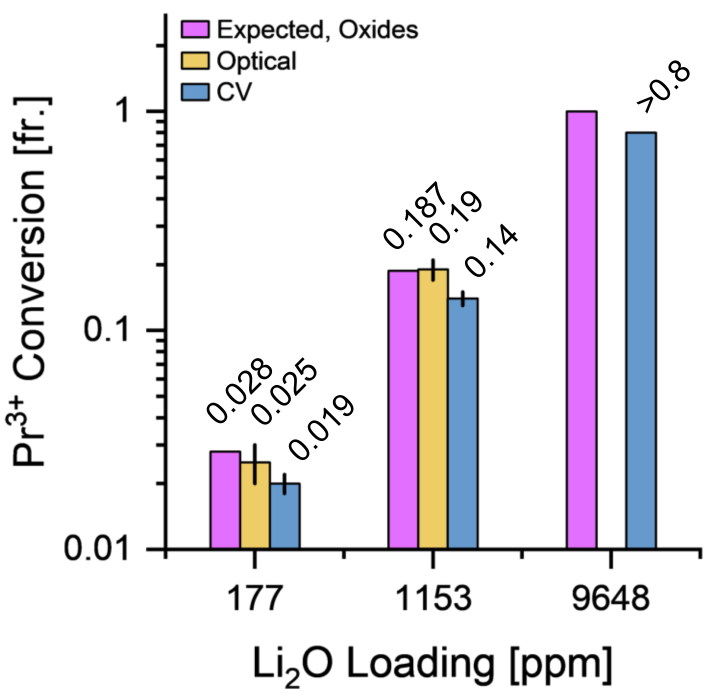

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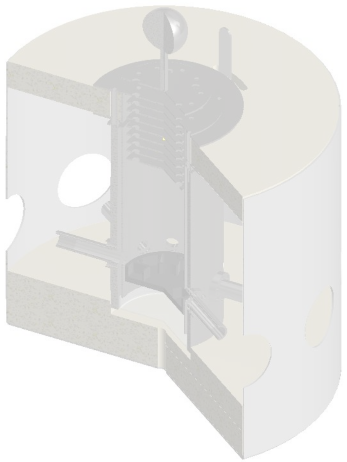
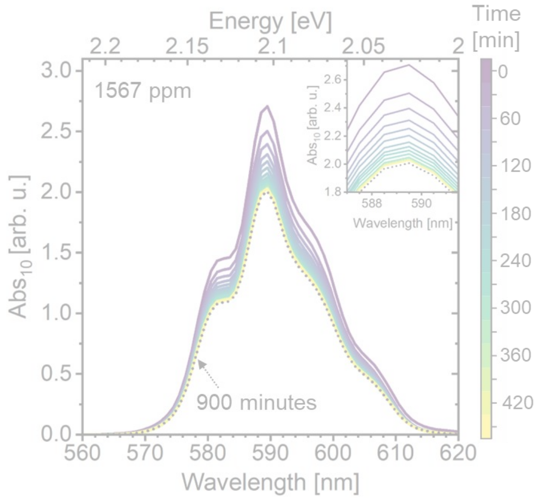
Conversion ratios match more closely with expected conversion of Pr^{3+} to predominantly oxide species

Conclusion remains tentative

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





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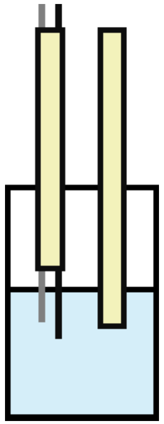
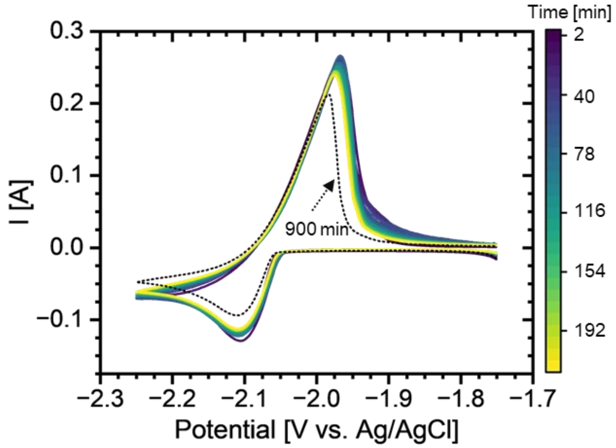
- Low loadings of O^{2-} product primarily oxychlorides

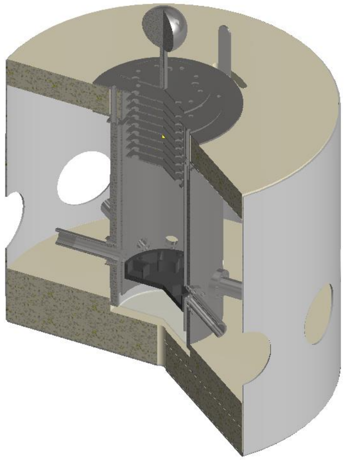
Track reaction of Pr^{3+} with O^{2-} using both absorption spectroscopy and electrochemistry

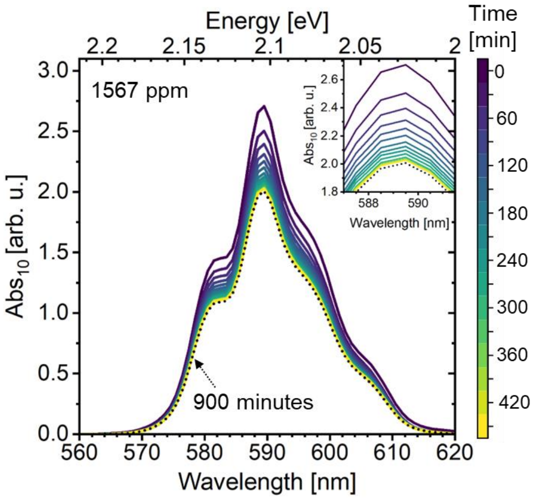




- Spectroscopy and electrochemistry provide complementary methods of analyte monitoring
  - Techniques point to similar conclusions
- Pr^{3+} suggested to react with O^{2-} to form primarily oxides

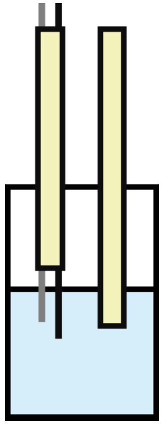
Track reaction of Nd^{3+} with controlled O^{2-} impurities: Absorption spectroscopy

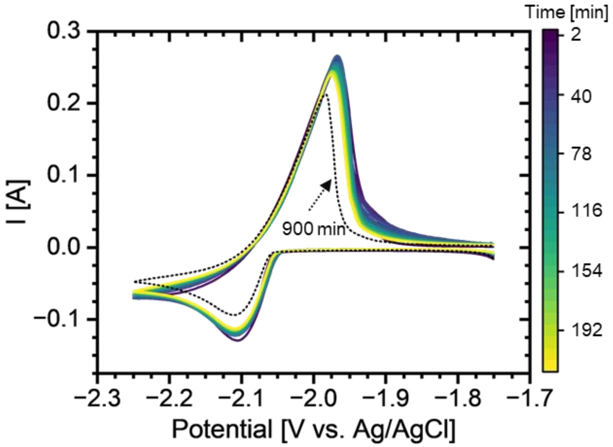




- Absorption spectroscopy works well to track Ln^{3+} concentrations in real-time
- Low loadings of O^{2-} product primarily oxychlorides

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
- Pr^{3+} suggested to react with O^{2-} to form primarily oxides

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

Thank you!

INL

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