Assessing Single Particle Electrocatalysts for Hydrogen Evolution in Neutral Media by Optically Monitoring Reaction Footprints

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Context

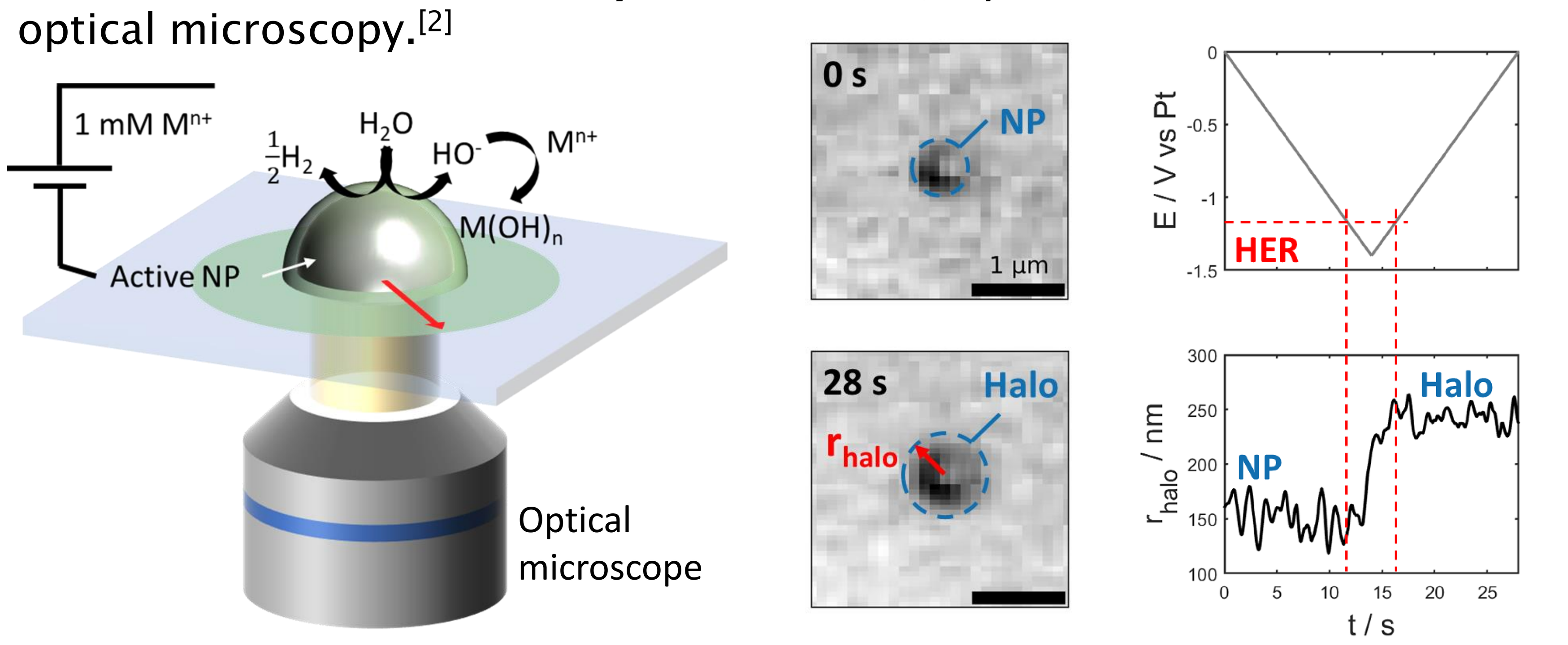
Investigating the electrocatalytic activity of **single nanoparticles** (NPs) is advantageous for at least two reasons:

1. In the absence of carbon and binders, it reveals their **intrinsic activity**.
2. It simplifies the establishment of **structure-activity relationships**.

In this context, **optical microscopies** hold the additional advantage of operating on hundreds of NPs at once. However, they rely on the visualization of markers. The most common ones are **gas nanobubbles** (NBs), which have the disadvantage of requiring extremely high current densities to nucleate.[1] Another option is to visualize the **pH gradient** generated by the reaction of interest, in this case the **hydrogen evolution reaction** (HER). While this can be done using fluorescent probes, it considerably limits the temporal resolution that can be achieved as substantial accumulation is required to generate a fluorescence microscopy image.

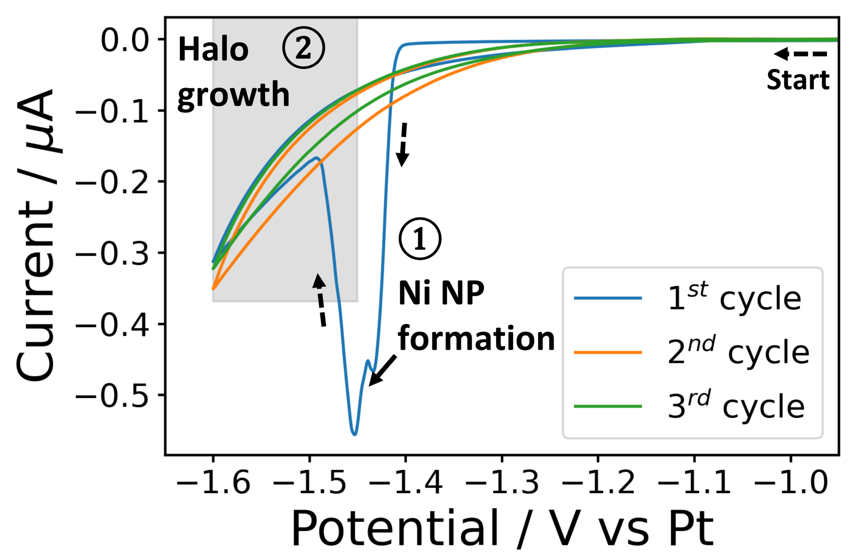
Principle

Instead, we propose here to visualize the pH gradient through the formation of an insoluble **hydroxide halo**, by refractive index-sensitive optical microscopy.[2]

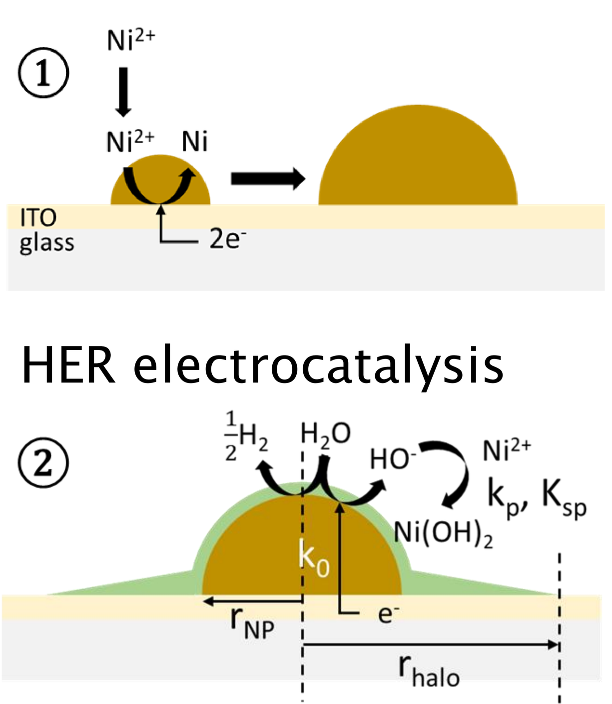


Case of Ni Nanoparticles

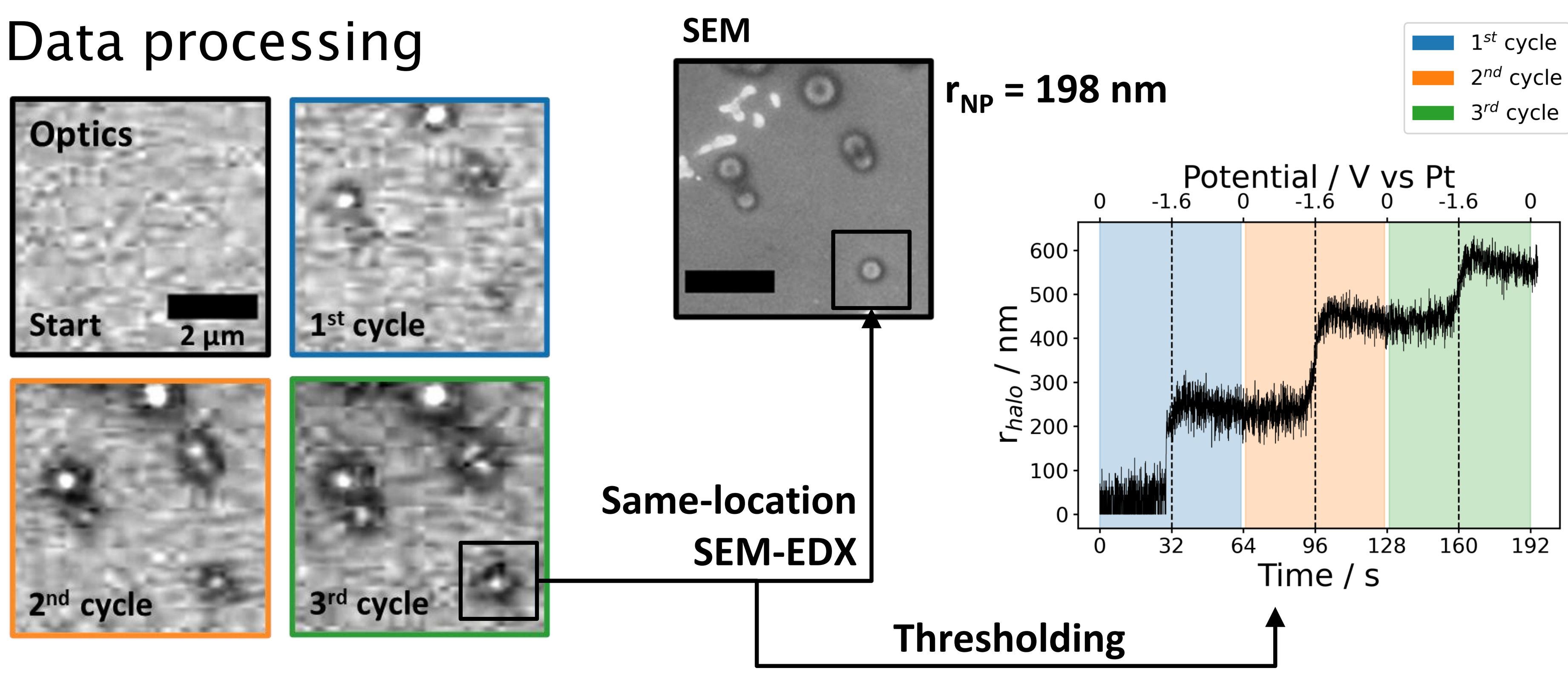
Electrochemistry



Electrodeposition[3,4]



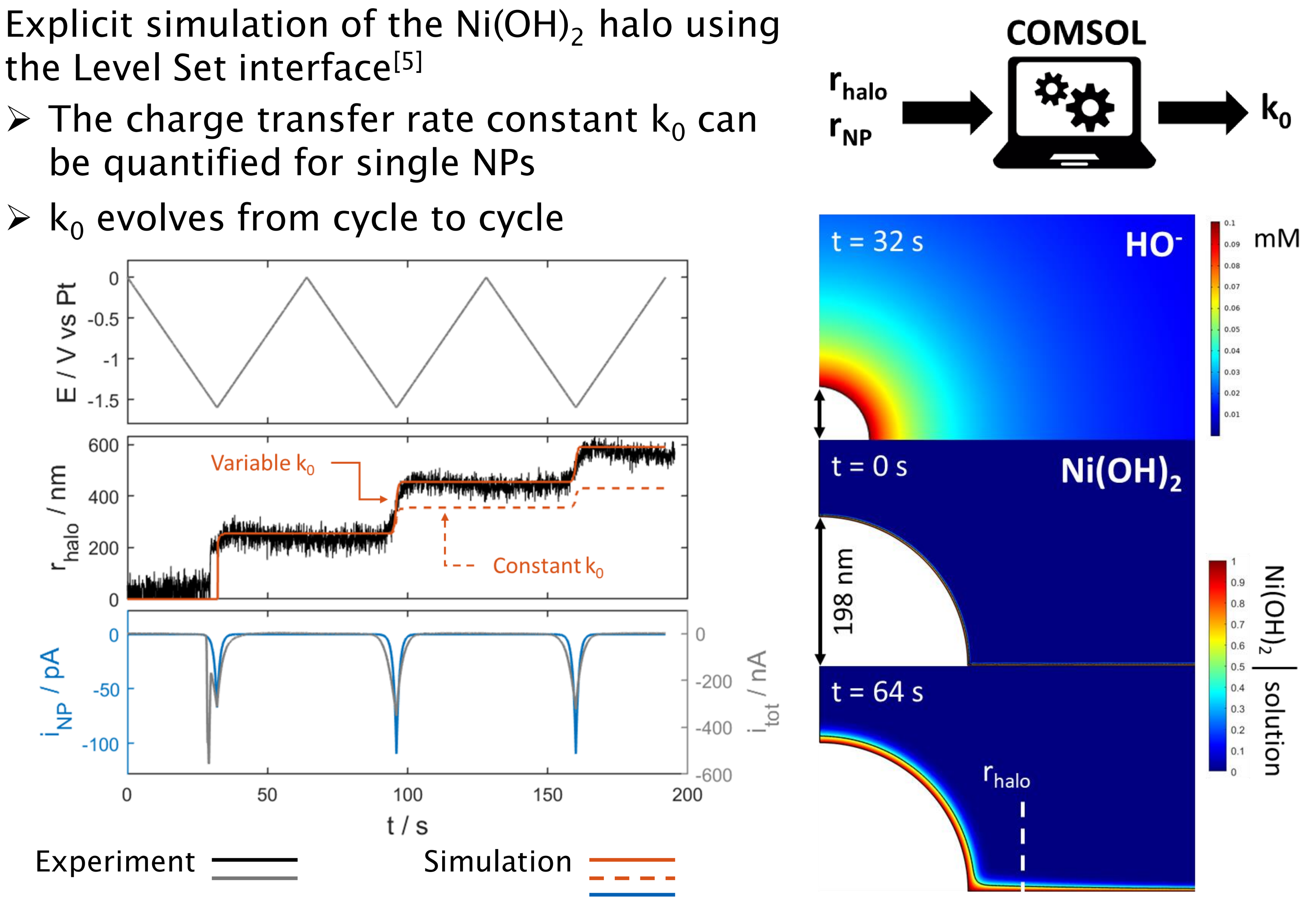
Data processing



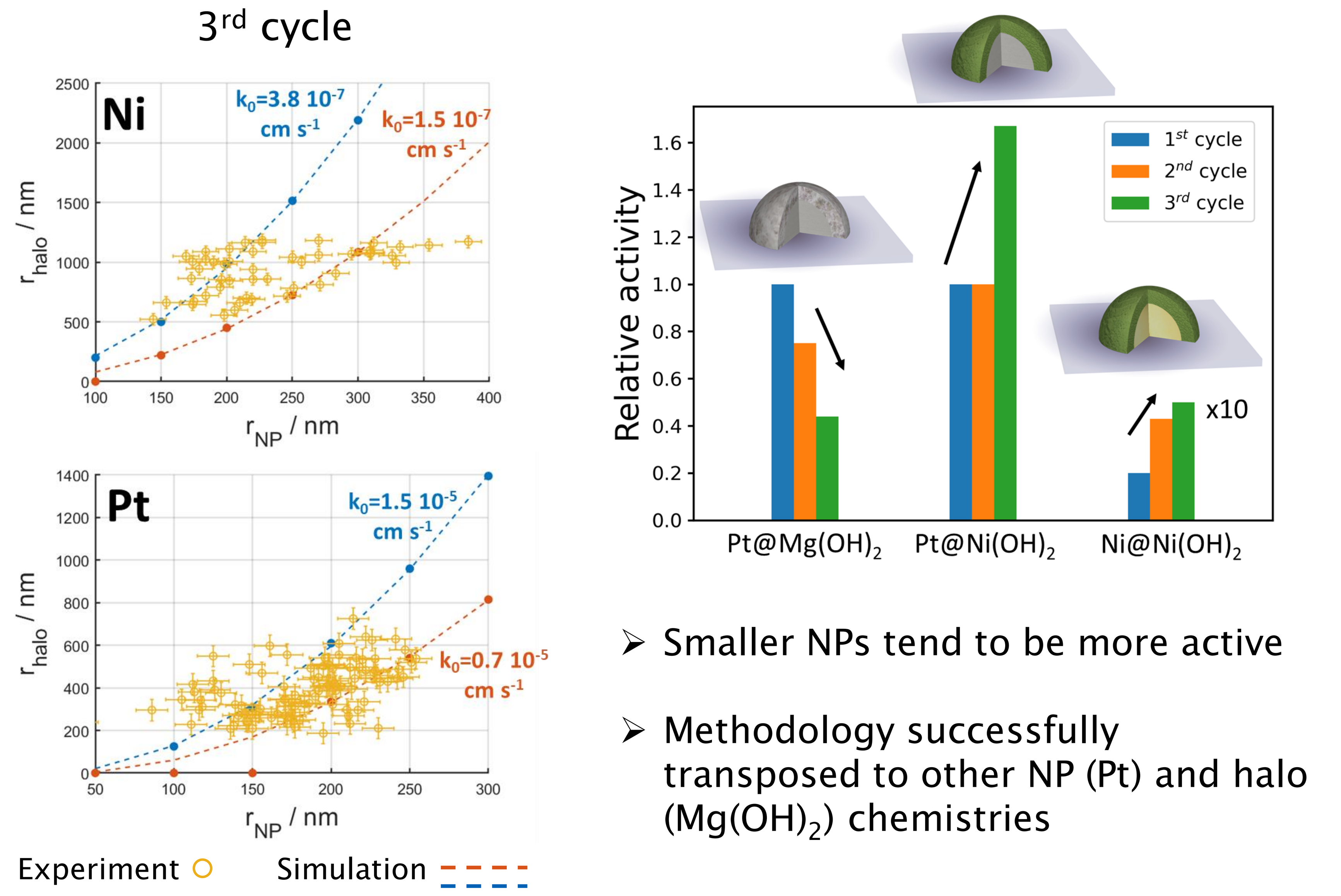
COMSOL Model

Explicit simulation of the $Ni(OH)_2$ halo using the Level Set interface[5]

- The charge transfer rate constant k_0 can be quantified for single NPs
- k_0 evolves from cycle to cycle



Size Effect and Versatility



- Smaller NPs tend to be more active
- Methodology successfully transposed to other NP (Pt) and halo ($Mg(OH)_2$) chemistries

Conclusions

- The HER activity of single NPs is evaluated at industrially relevant current densities, without using H_2 NBs as markers.
- The results highlight a size effect and the specific role of $Ni(OH)_2$ in enhancing the HER activity of Ni and Pt as previously reported.[6]
- The methodology is transposable to most electrocatalytic reactions of interest for energy conversion applications, not only to gas evolution reactions, as most of them involve protons (e.g., CO_2RR or ORR).
- It is also transposable to any microscopy technique able to detect the hydroxide halo *in situ* (e.g., AFM or TEM).

References

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