EXAFS Study of PtRu Core-Shell Nanoparticles as Electrocatalysts for DMFC's

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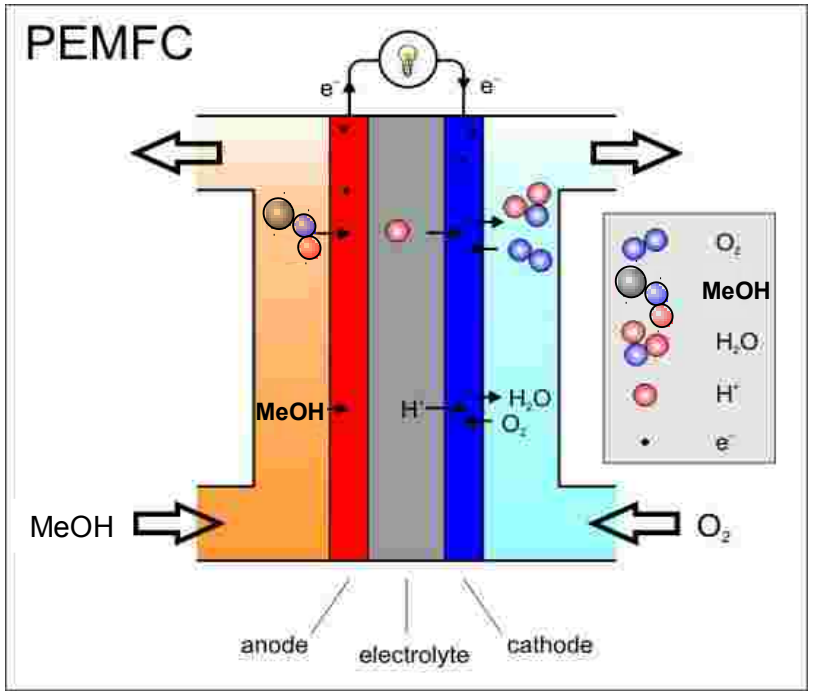
Sponsors: Department of Energy & Department of Education

Outline

- Direct methanol fuel cells
- Synthesis of core-shell nanoparticles
- Electrochemical characterization
- *In situ* XAFS experiments
- Ru XAFS results & conclusions

Polymer exchange membrane fuel cell



Anode: $E^{o}_{anode} = 0.016$ V

$$CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^-$$

Cathode: $E^{o}_{cathode} = 1.23$ V

$$3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

Overall: $E^{o}_{cell} = 1.214$ V

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$

Bi-functional mechanism for CO oxidation

$$Pt\text{-}(CO)_{ads} + Ru\text{-}OH \longrightarrow Pt + Ru + CO_2 + H^+ + e^-$$

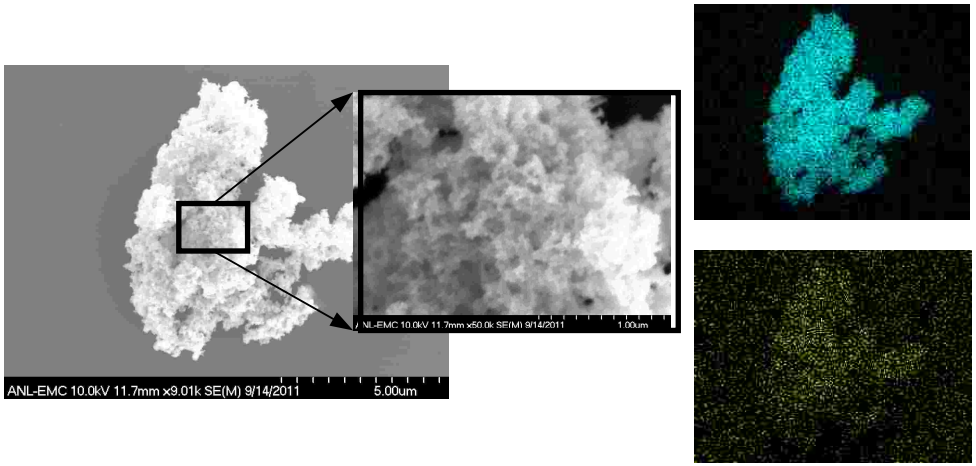
U.S. Department of Defense (DoD) Fuel Cell Test and Evaluation Center (FC*Tec*)

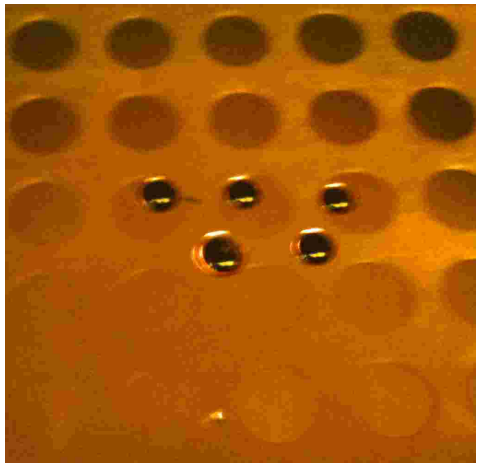
Role of Ru

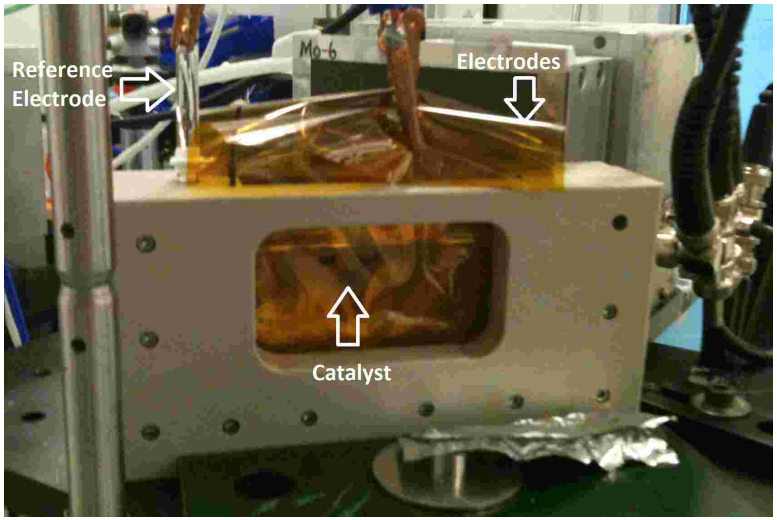
- Methanol oxidation rate using pure Pt is sluggish
- CO tolerance is poor
- PtRu bifunctional catalyst improves performance
  - In commercial PtRu catalysts there is always a lot of inactive Ru-oxide
  - Ru signal dominated by metallic Ru environment
  - How does Ru behave in the presence of reactants adsorbed on platinum surface?

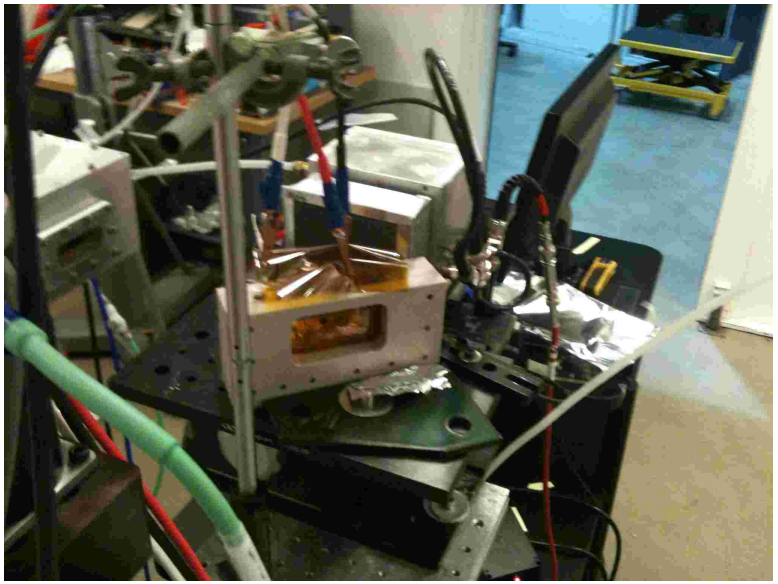
Core-shell nanoparticles can resolve these

Ru-decorated Pt nanoparticles

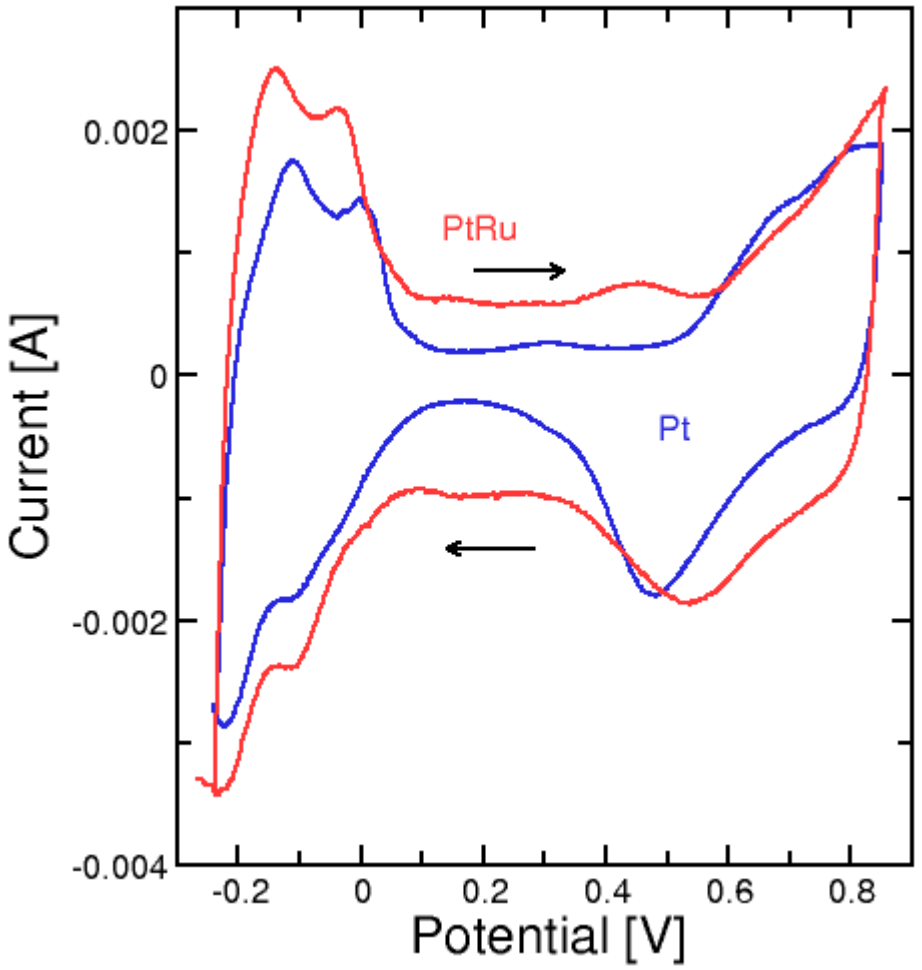








Electrochemical performance no methanol

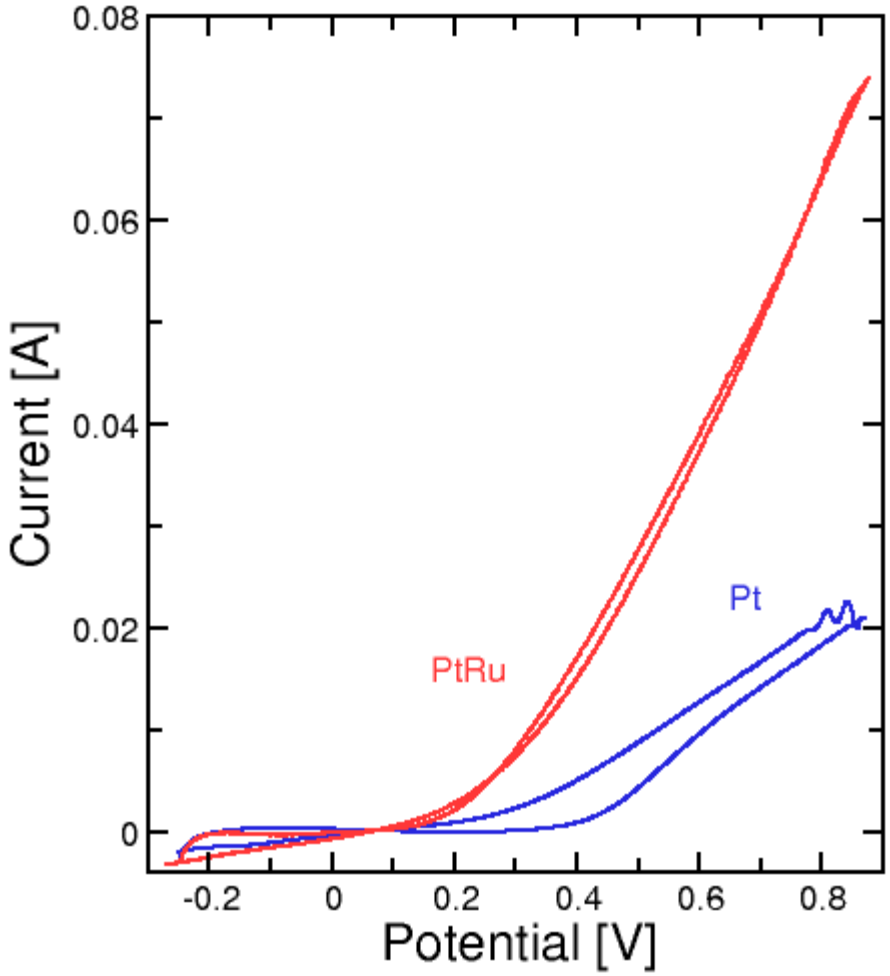


Low V peaks are H^+ stripping with visible peaks for (111), (110), & (100) faces

Dip ~0.5V is oxygen stripping from Pt surface (and Ru)

Ru on surface shifts potential of all peaks

Electrochemical performance with methanol

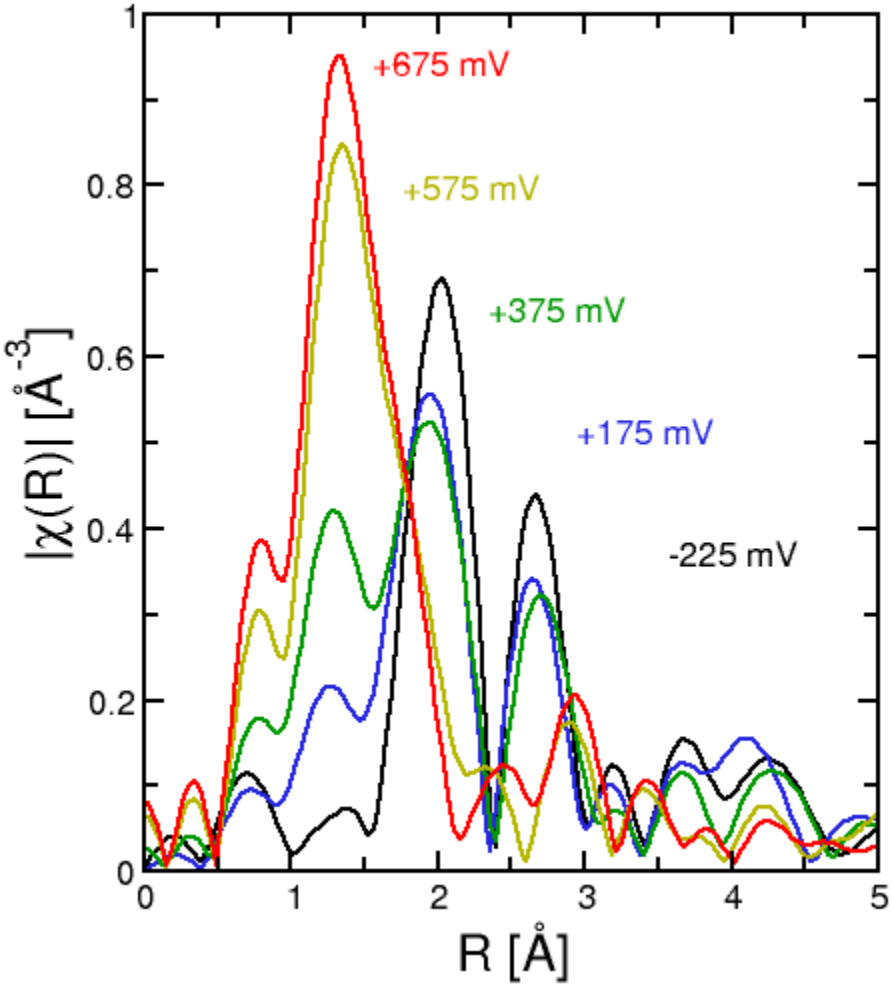


Current rise due to methanol oxidation

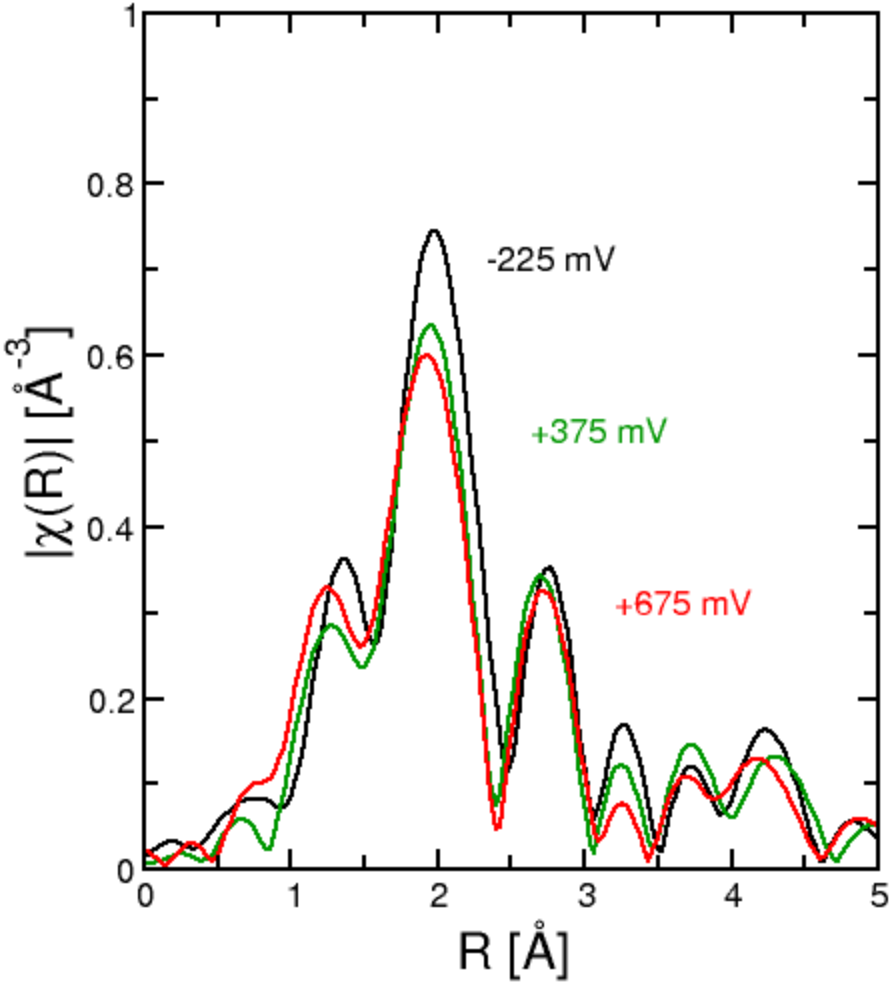
Ru shifts “turn on” point to lower potential by removing the CO which blocks active sites on Pt surface

Ru EXAFS

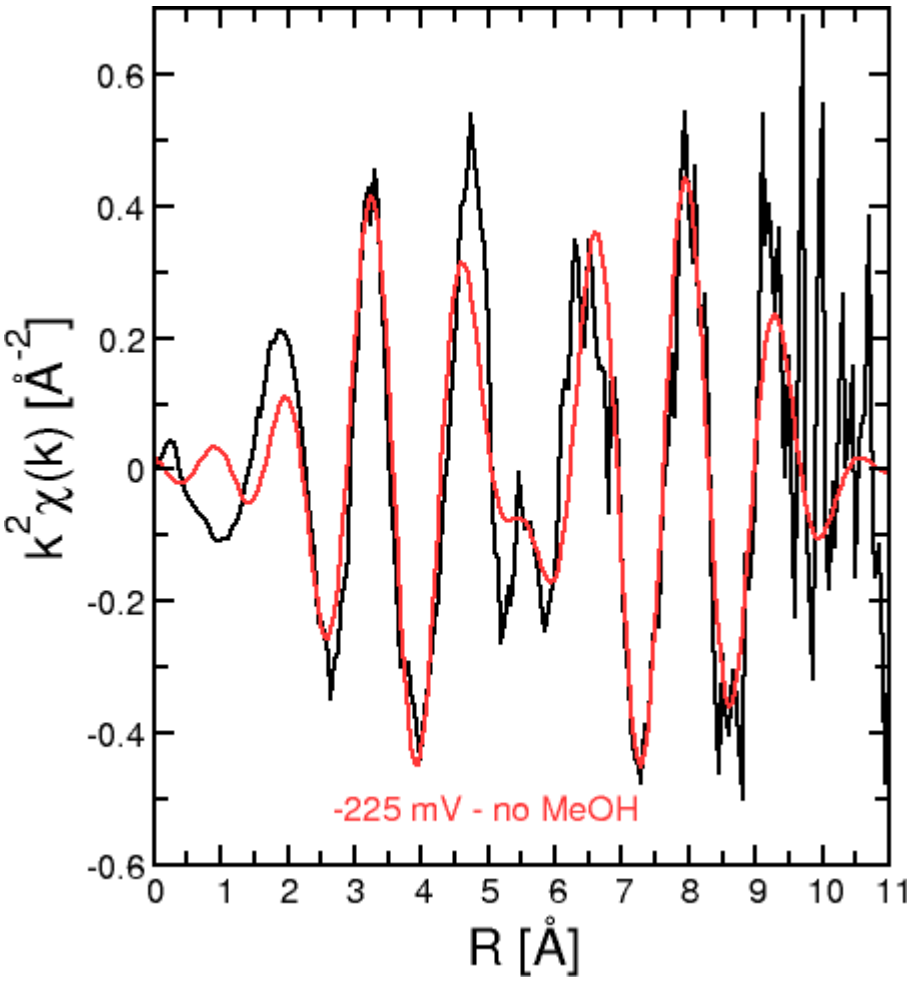
No methanol

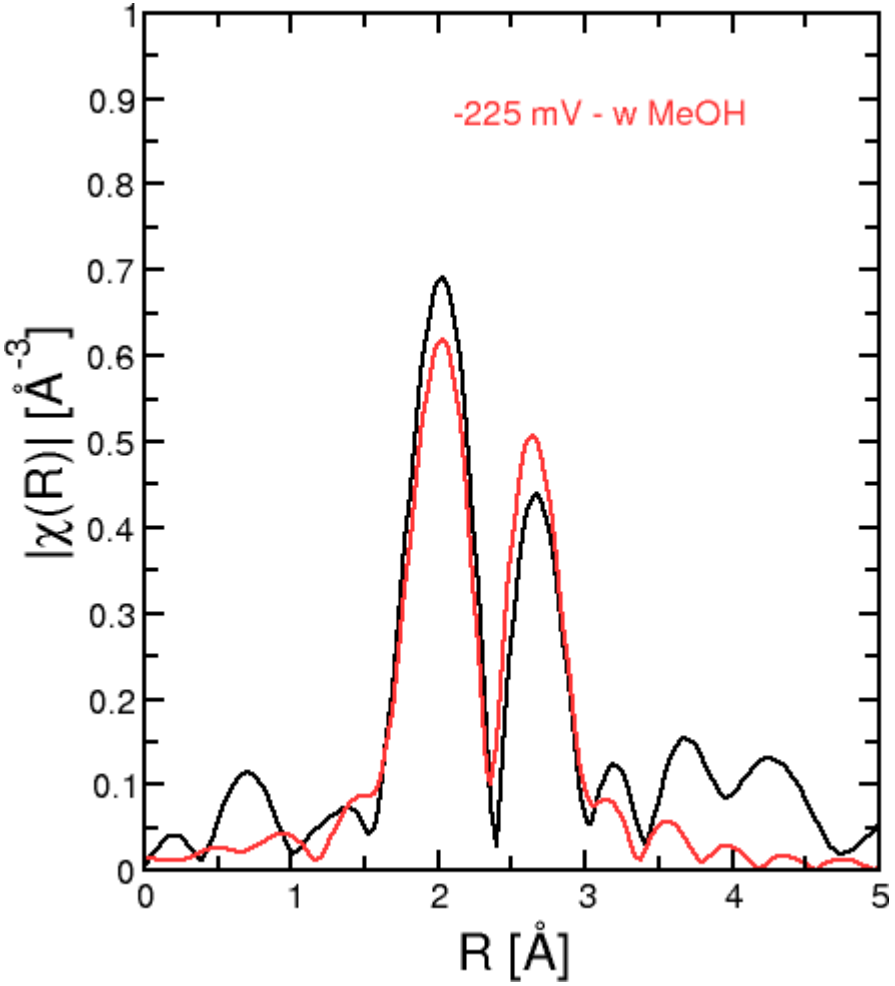


With methanol



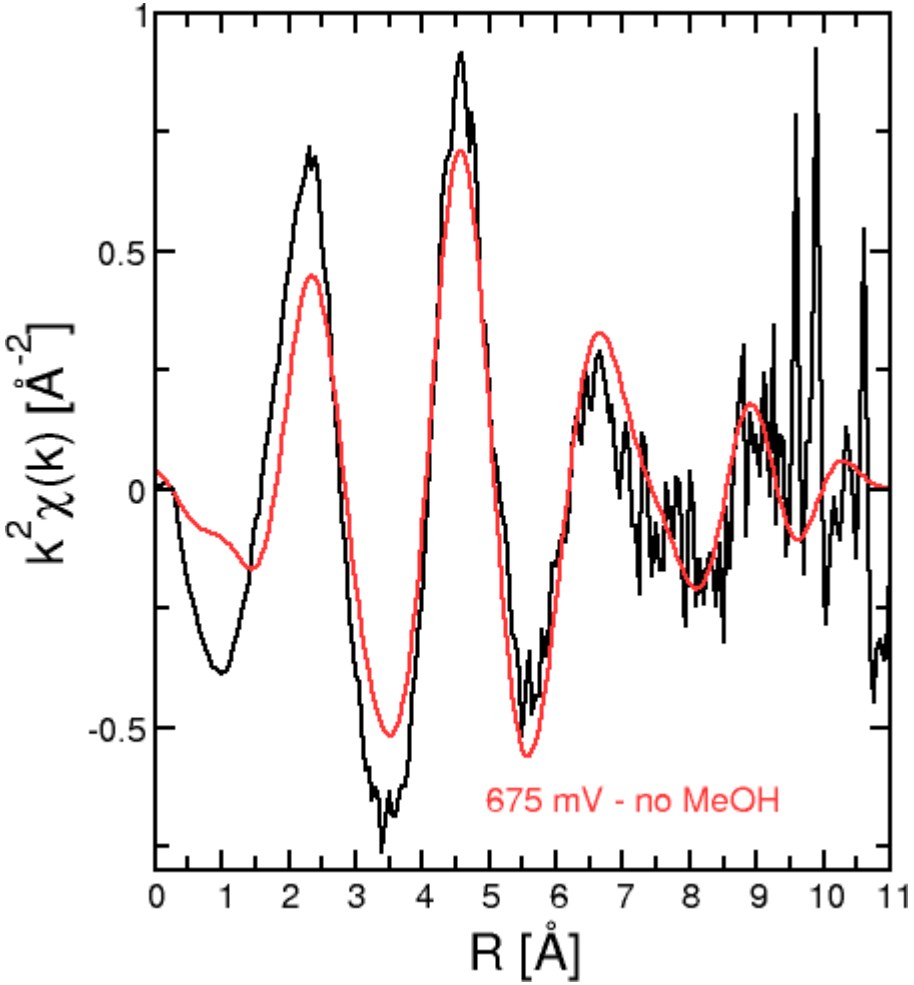
Fit Example: -225 mV without MeOH

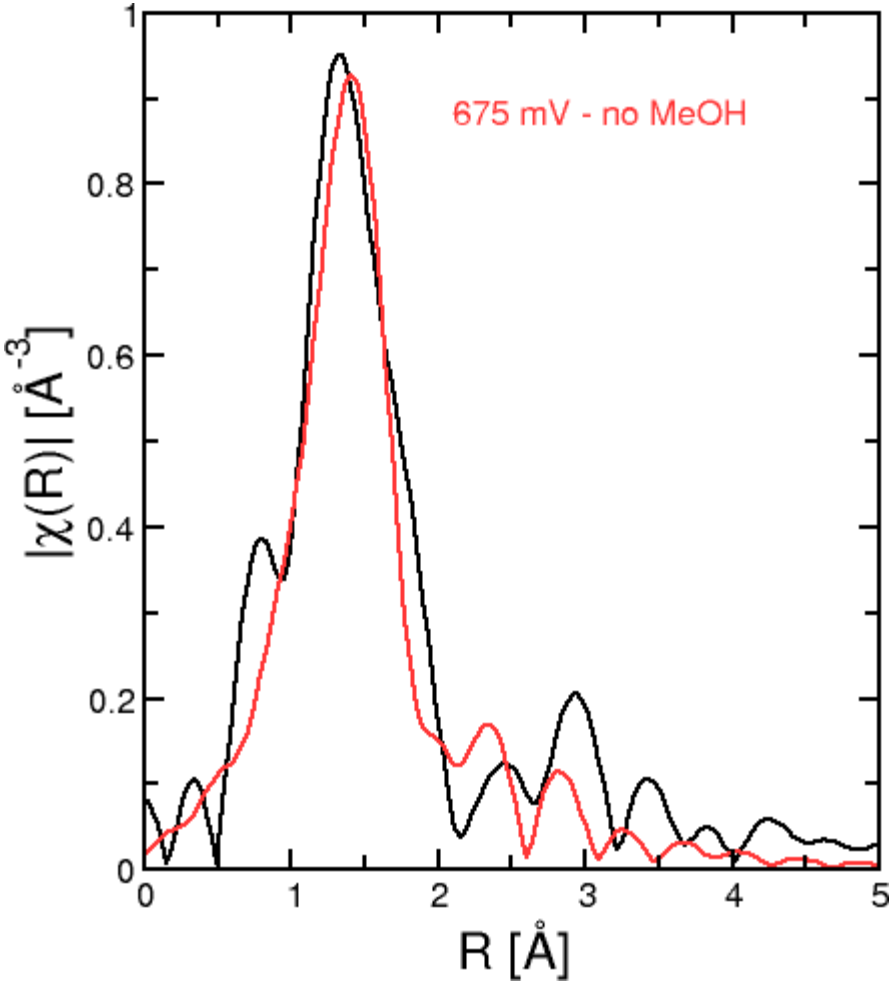




short Ru-Pt path long Ru-Pt path Ru-Ru path

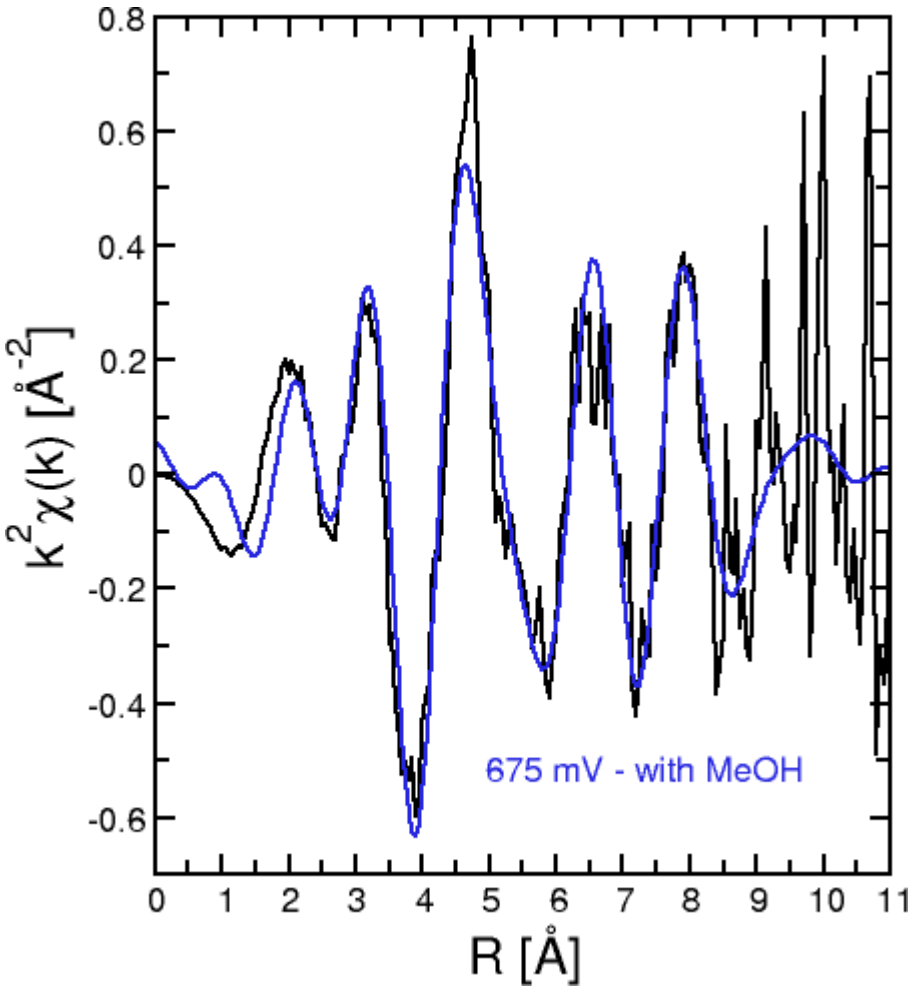
Fit Example: 675 mV without MeOH

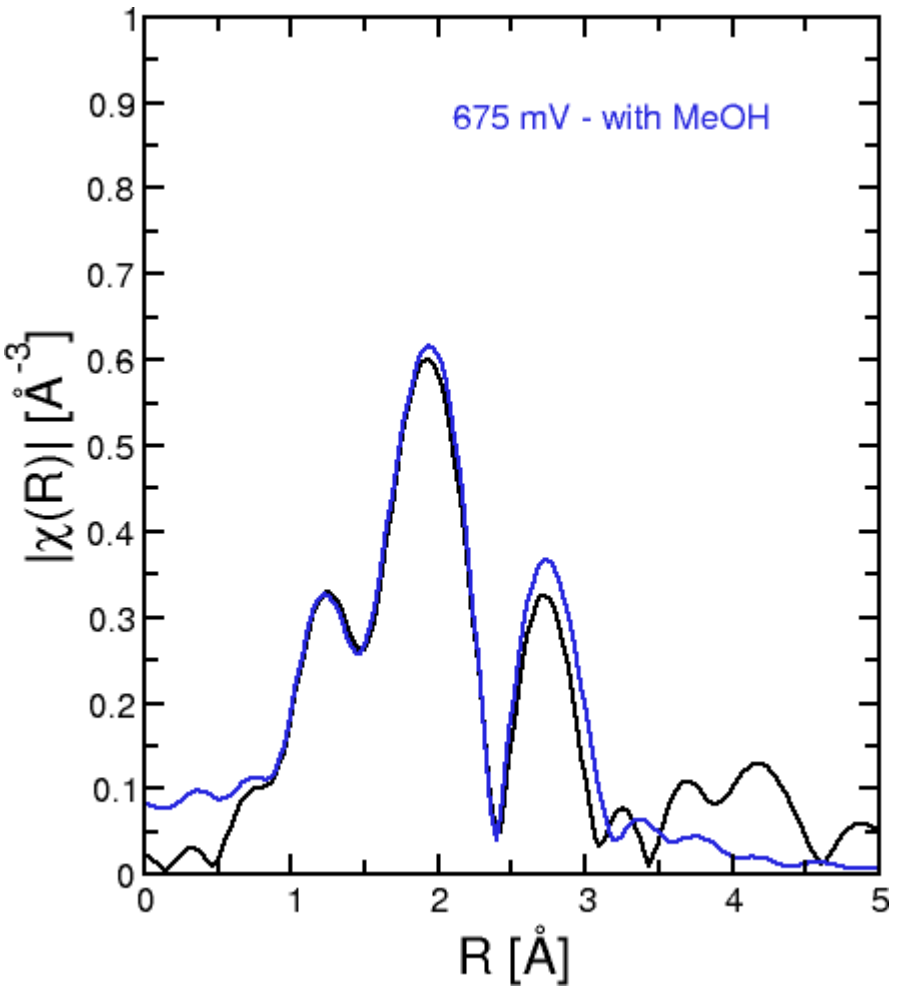




four RuO_2 paths long Ru-Pt path

Fit Example: 675 with MeOH

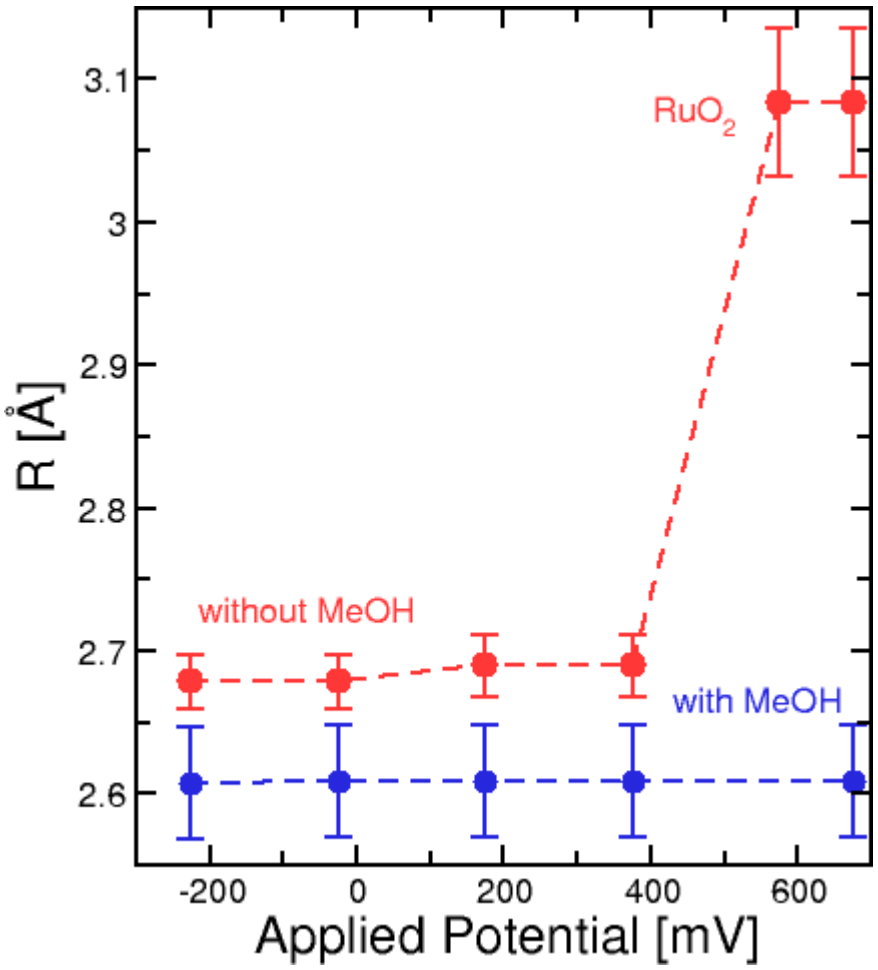




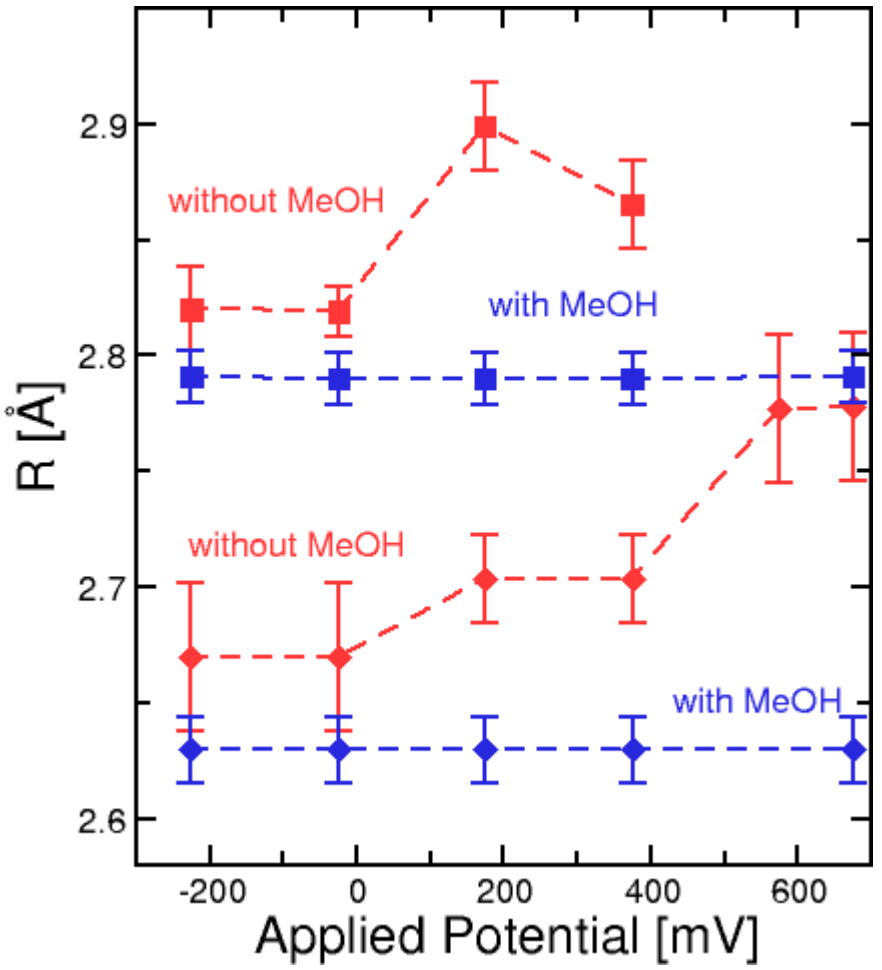
short Ru-Pt path long Ru-Pt path Ru-Ru path Ru-O path short Ru-O/C path

Ru-M path evolution

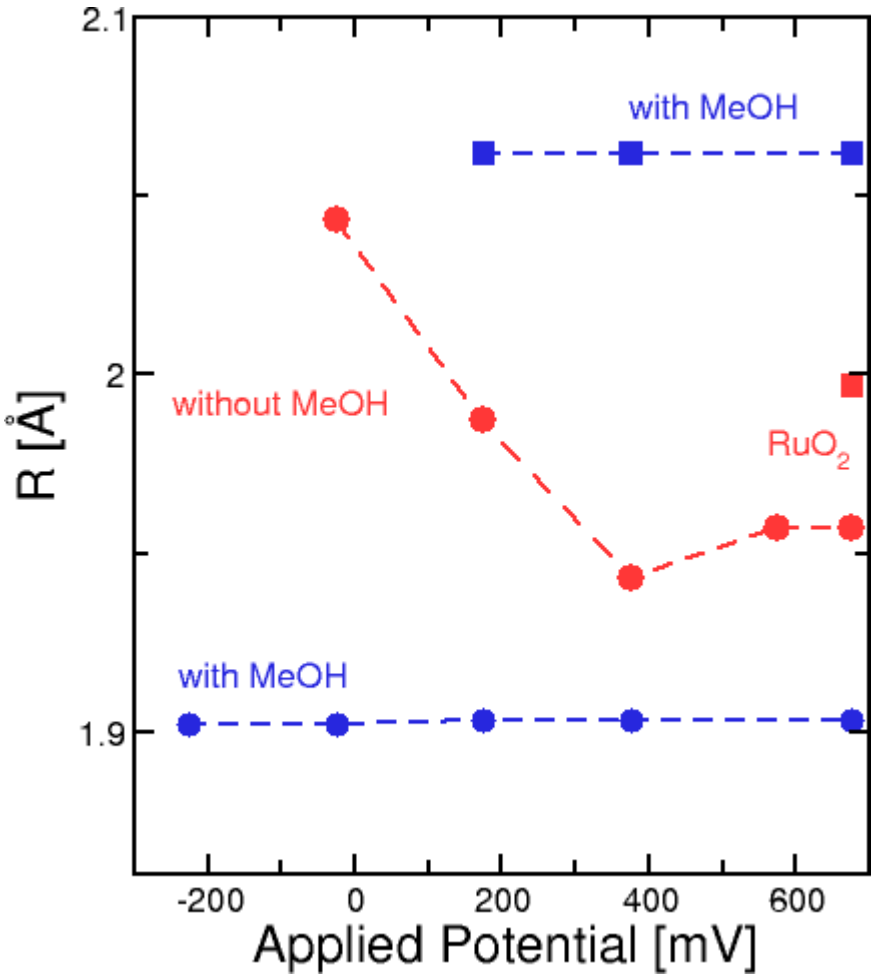
Ru-Ru path



Ru-Pt paths



Fitting results



Without methanol

Ru is metallic with Pt and Ru neighbors at low V
Pt/Ru @ 2.67Å & Pt @ 2.84Å

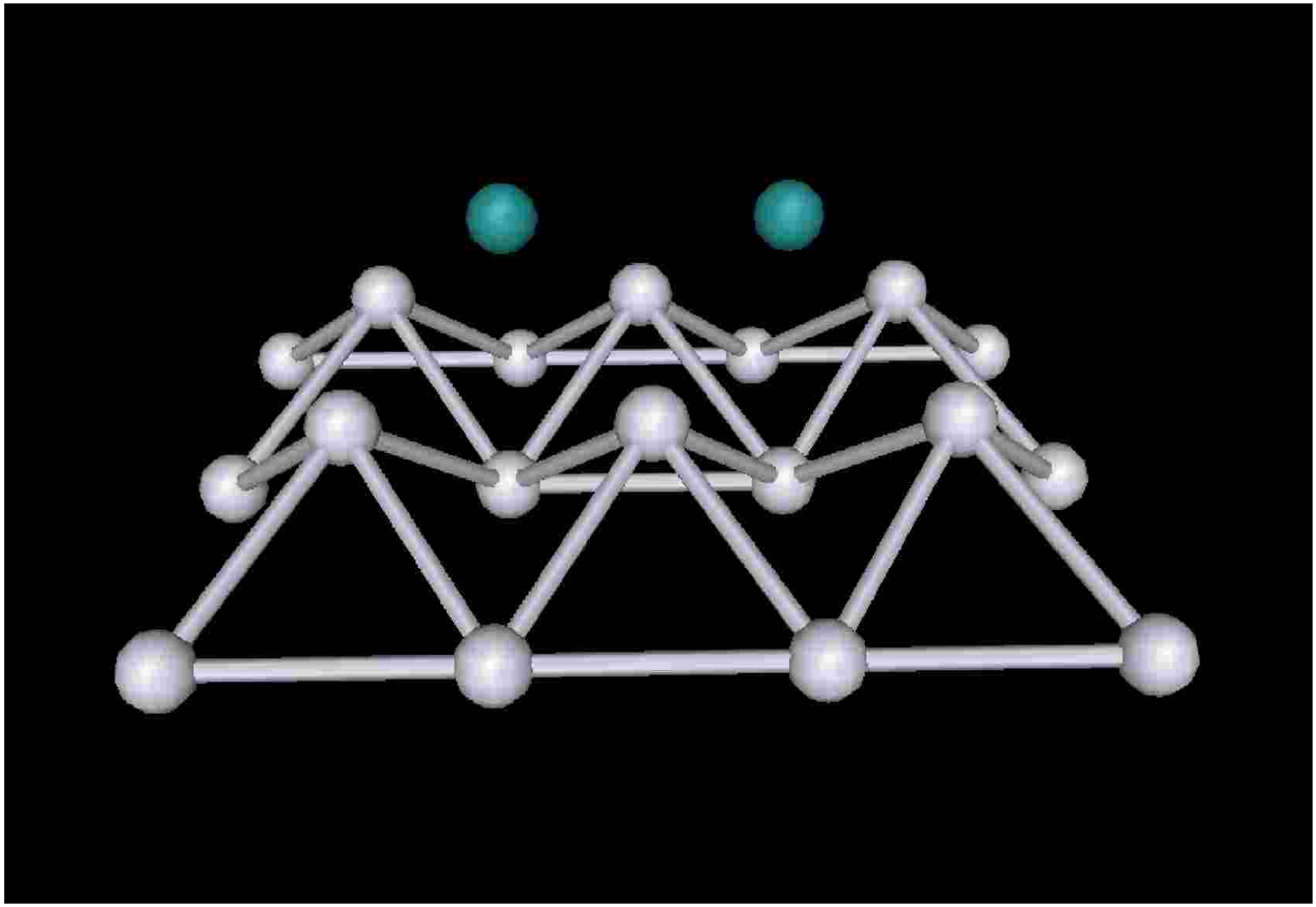
Ru oxidizes completely above 375 mV all metal distances increase or disappear O @ 1.95Å & 1.99Å

With methanol

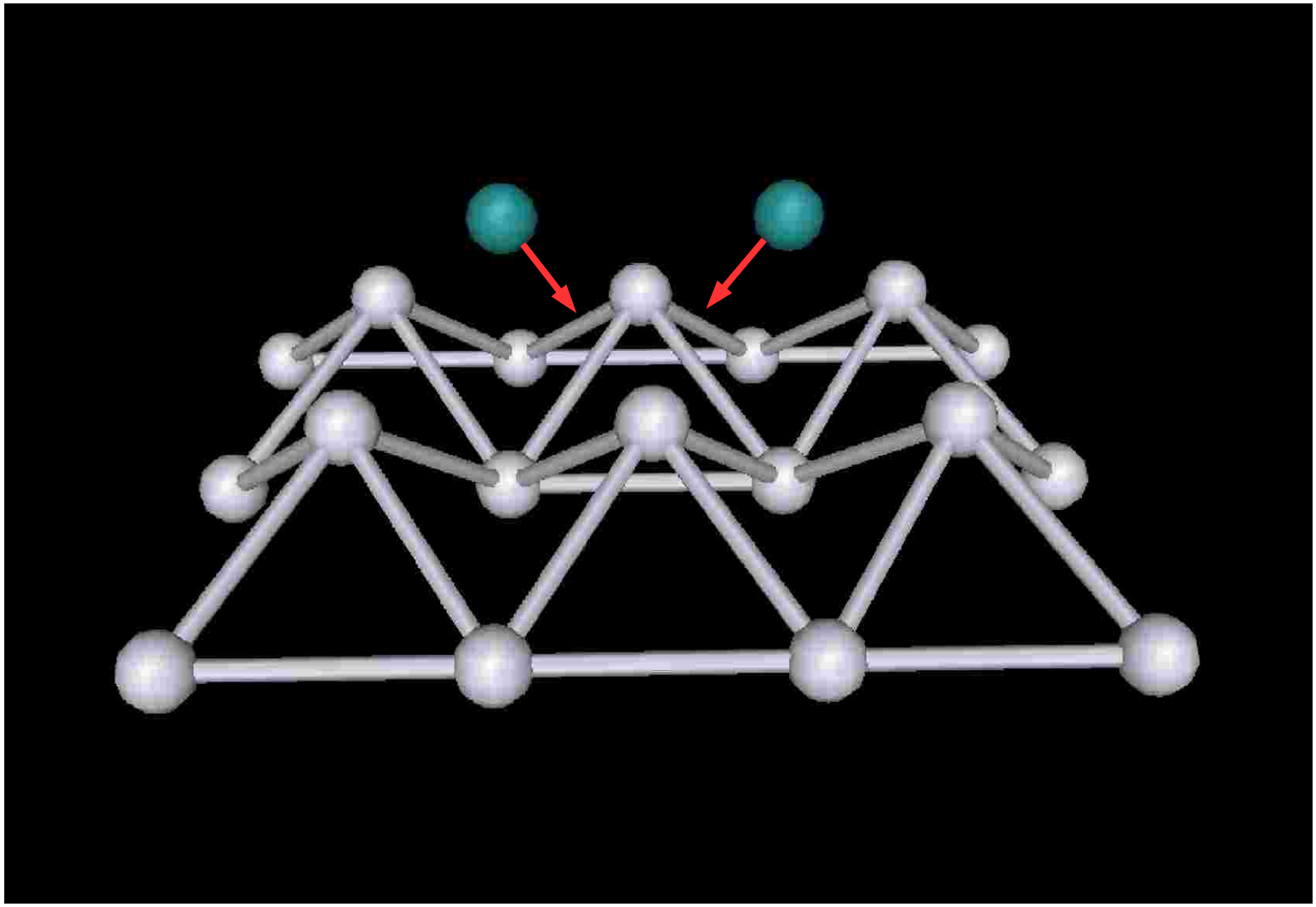
Ru is more metallic with Pt and Ru neighbors at all V
Pt/Ru @ 2.62Å & Pt @ 2.79Å

Ru has a low Z neighbor above 175 mV (CO, OH?) C or O @ 2.06Å

Surface rearrangement



Surface rearrangement



Thank you!

- Collaborators
  - Christopher Pelliccione – IIT (Ph.D. Student)
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