Pt versus Fe single site catalyst models for oxygen reduction reaction: an EC-STM investigation on metal octaethylporphyrins

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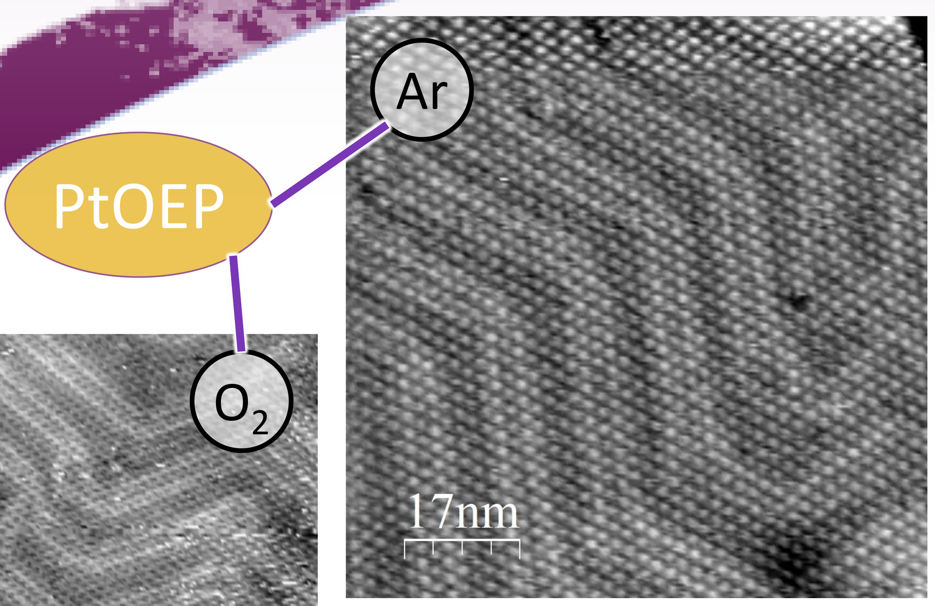
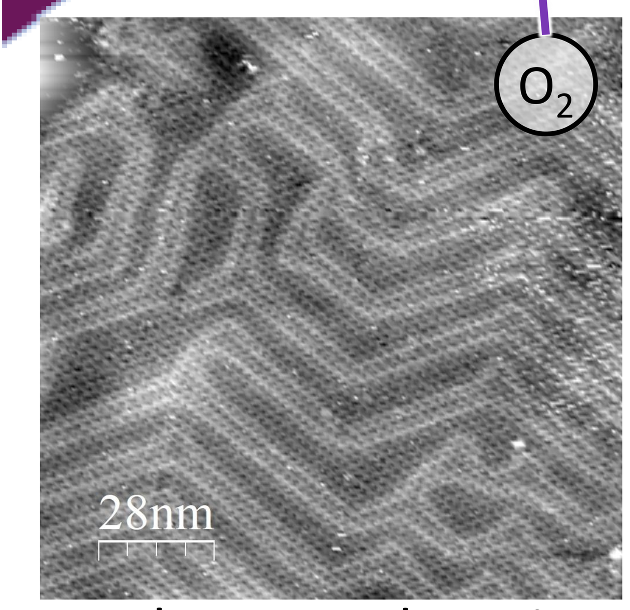
Introduction

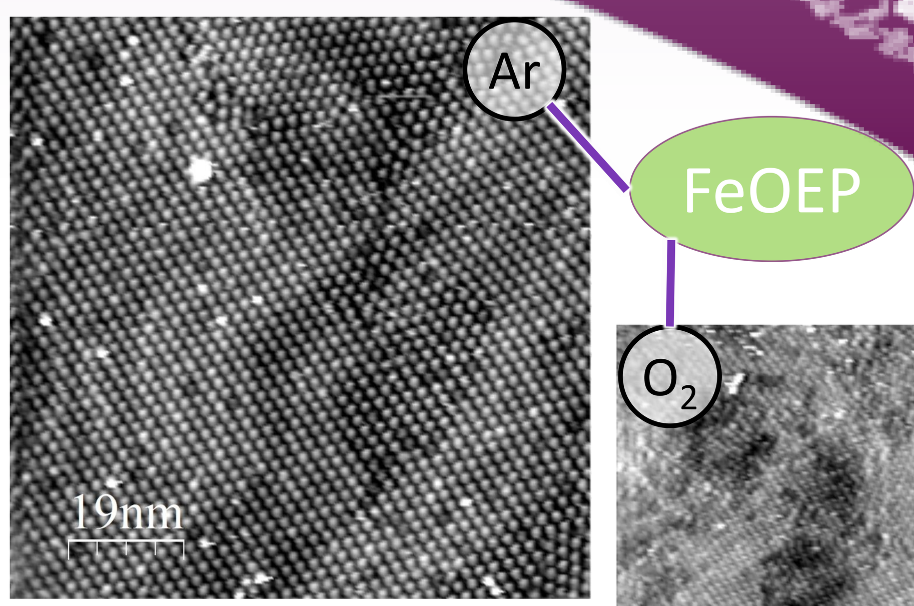
FeN_x-based carbons are promising materials for replacing Pt as catalysis for ORR in PEM-fuel cells and metal-air batteries. ORR was studied at the molecular scale thanks to EC-STM, evaluating behavior and performances of PtN_4 and FeN_4 sites, featured in the parent metal-octaethylporphyrin.

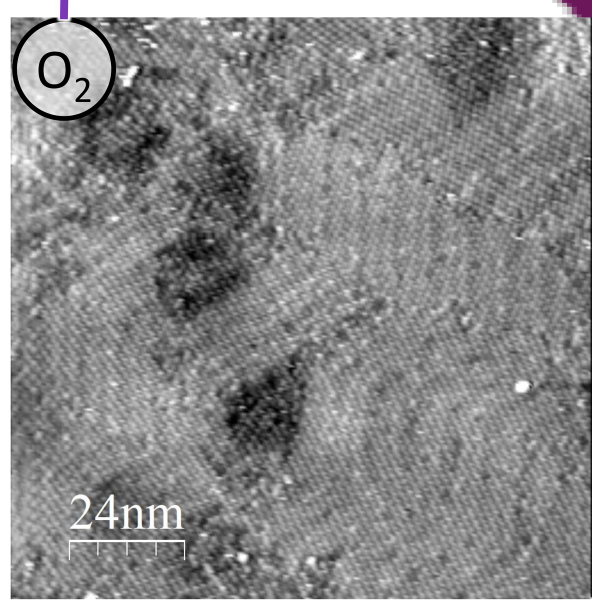




EC-STM images of PtOEP layers in Ar- and O_2-saturated electrolyte.

π electron donation ability of PtOEP stabilises herringbone reconstruction.



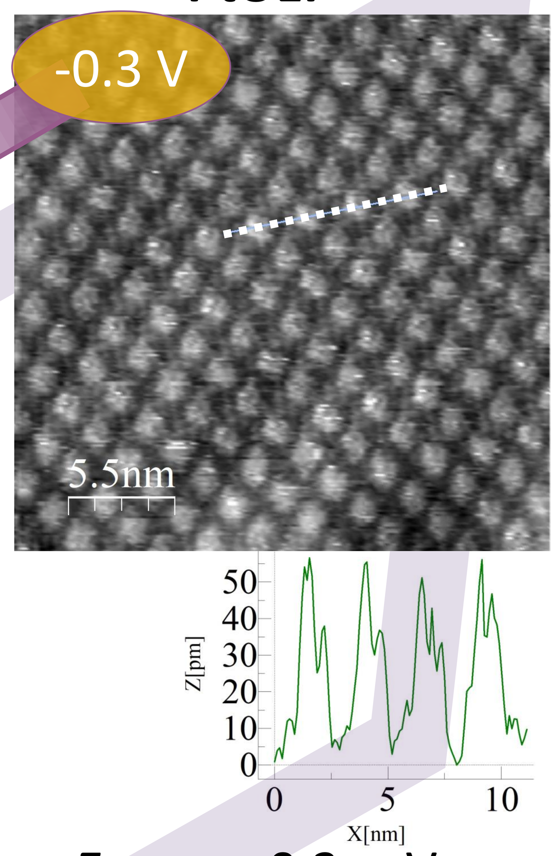


EC-STM images of PtOEP layers in Ar- and O_2-saturated electrolyte.

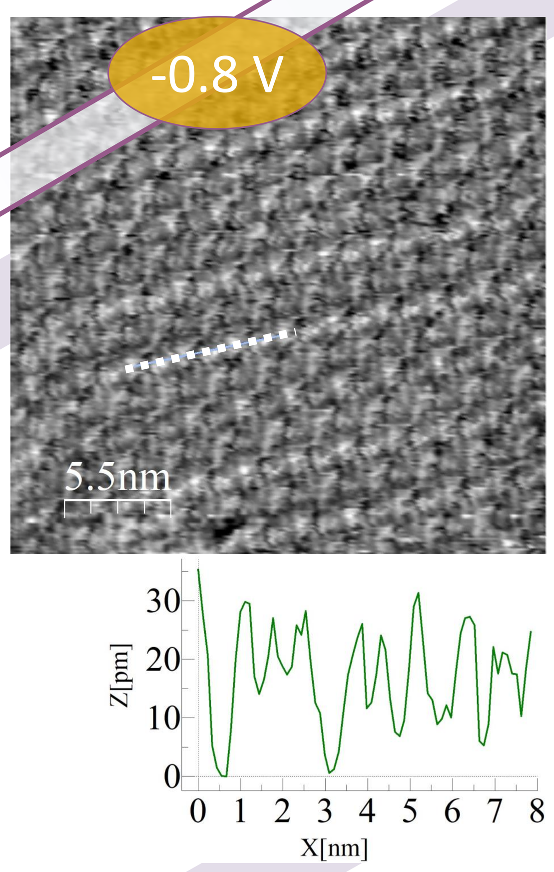
π electron donation acts also with FeOEP.

Potentiodynamic imaging

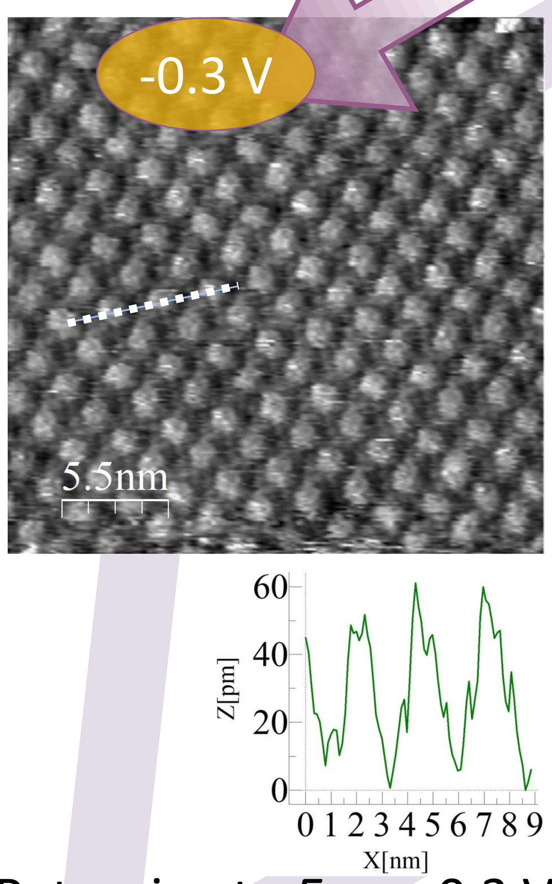
PtOEP



At E_{app}= -0.3 V, a protrusion of ~60 pm indicates O_2 adsorption.

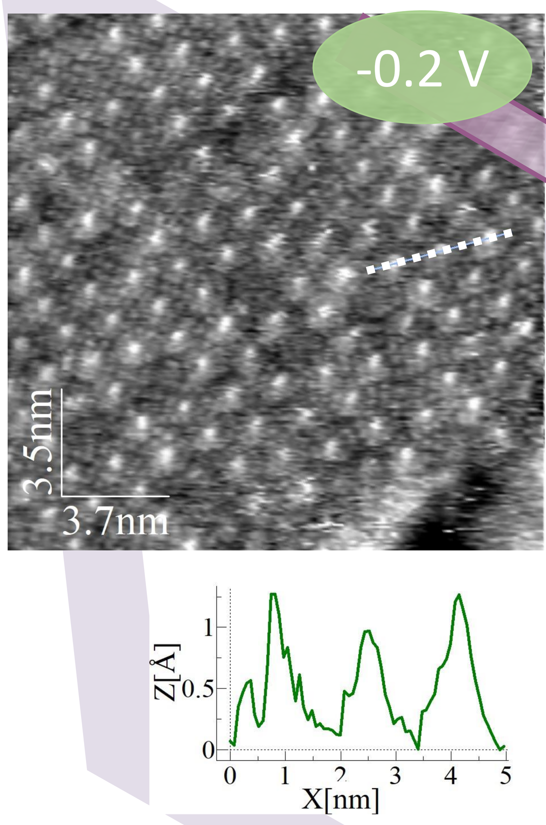


At E_{app}= -0.8 V, the protrusion is lost and ORR is occurring.

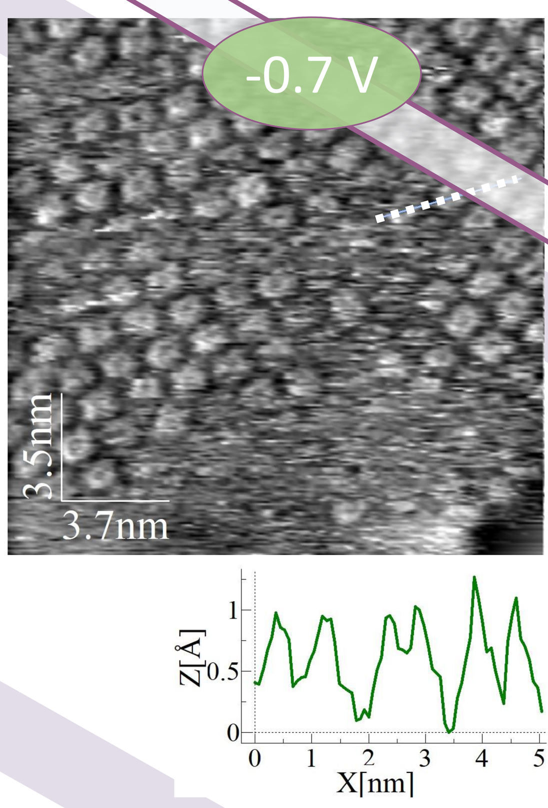


Returning to E_{app}= -0.3 V, the protrusion is restored.

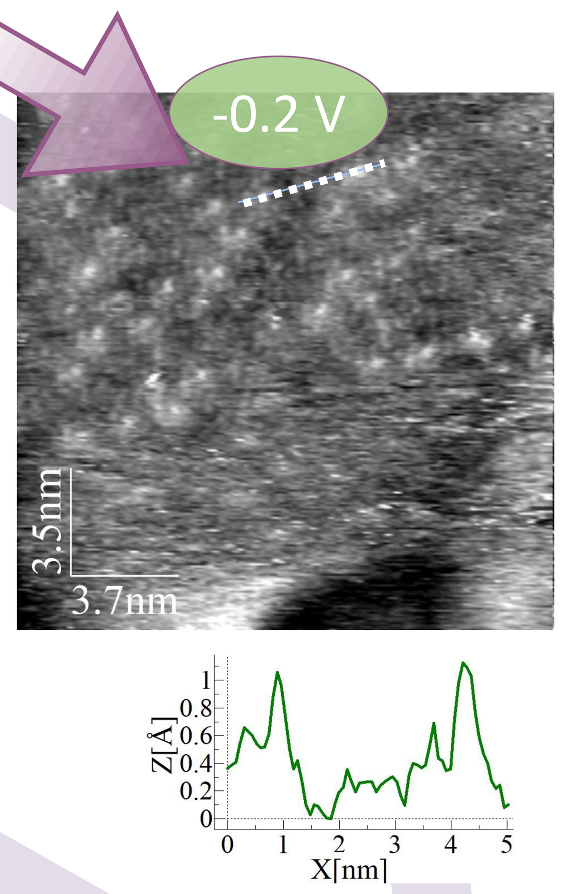
FeOEP



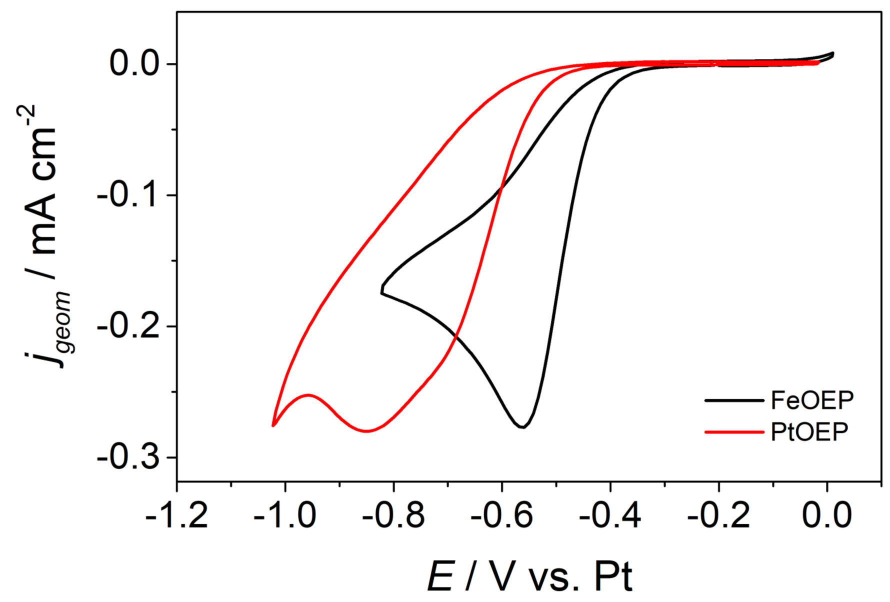
At E_{app}= -0.2 V, a protrusion of ~80 pm indicates O_2 adsorption.

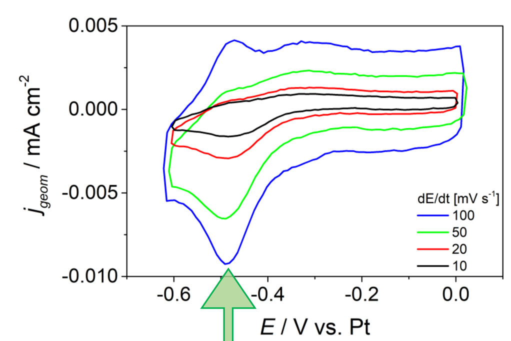


At E_{app}= -0.7 V, the protrusion disappears and dim spots appear in the centre.



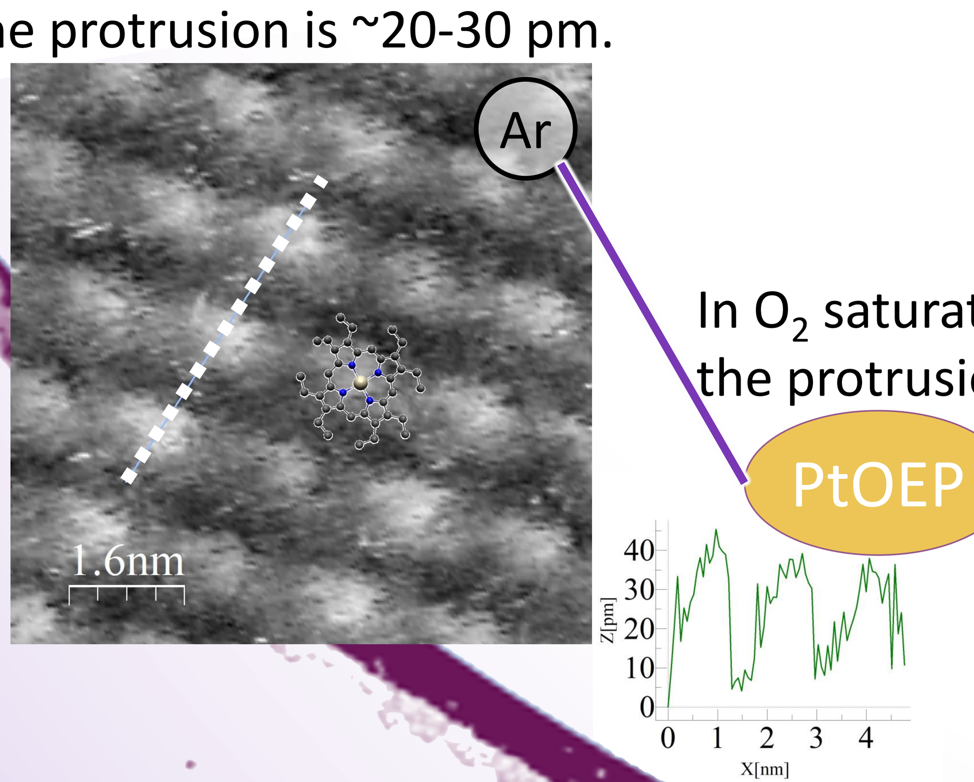
Returning to E_{app}= -0.2 V, the protrusion is restored, few dim spots remain and the layer is partially damaged.



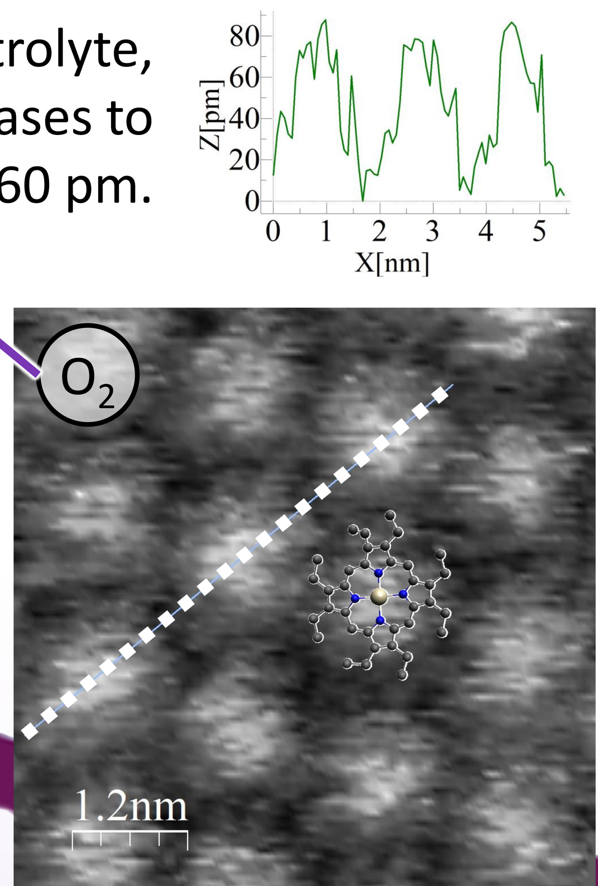


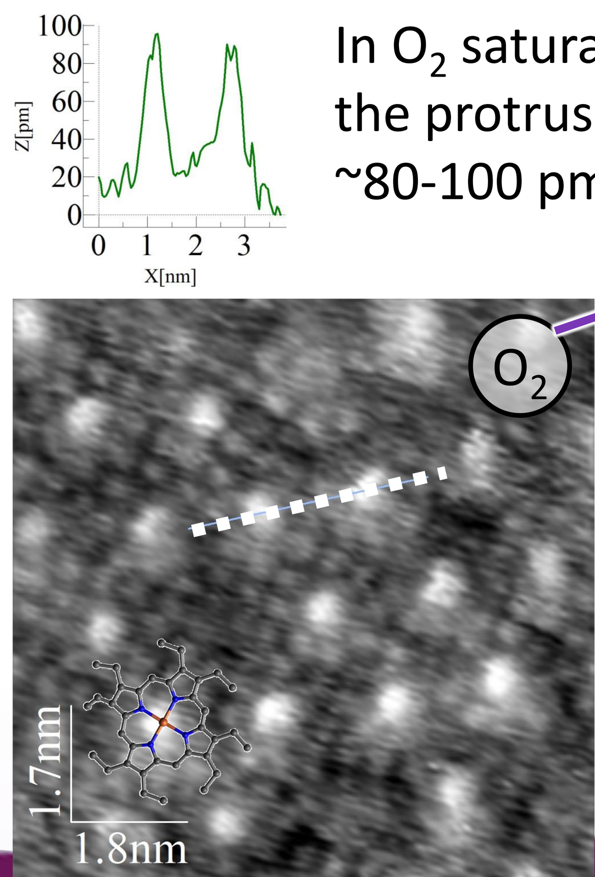
Both PtOEP and FeOEP are catalytically active towards ORR. PtOEP is significantly less performing of ~400 mV than FeOEP. FeOEP reduces O_2 thanks to the “redox catalysis”.

PtOEP adlayer in Ar saturated electrolyte. The protrusion is ~20-30 pm.



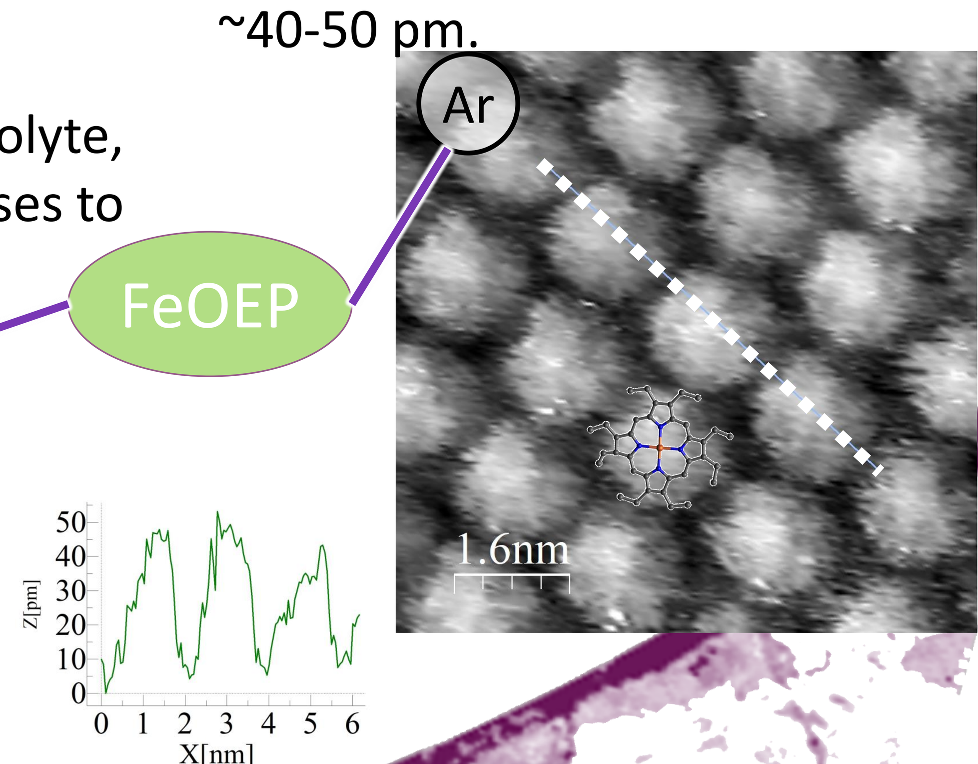
In O_2 saturated electrolyte, the protrusion increases to ~40-60 pm.





In O_2 saturated electrolyte, the protrusion increases to ~80-100 pm.

FeOEP adlayer in Ar saturated electrolyte. The protrusion is ~40-50 pm.



Conclusion

The combined EC-STM / cyclic Voltammetry investigation revealed a substantial difference in ORR catalysis for PtOEP and FeOEP. For FeOEP, a redox catalysis occurs, while the real catalytic process (though weak) must be clarified for PtOEP.