

## Ru@Pt Core-Shell Catalysts for the Oxygen Reduction Reaction (ORR), a New Framework for Tuning Binding Energies

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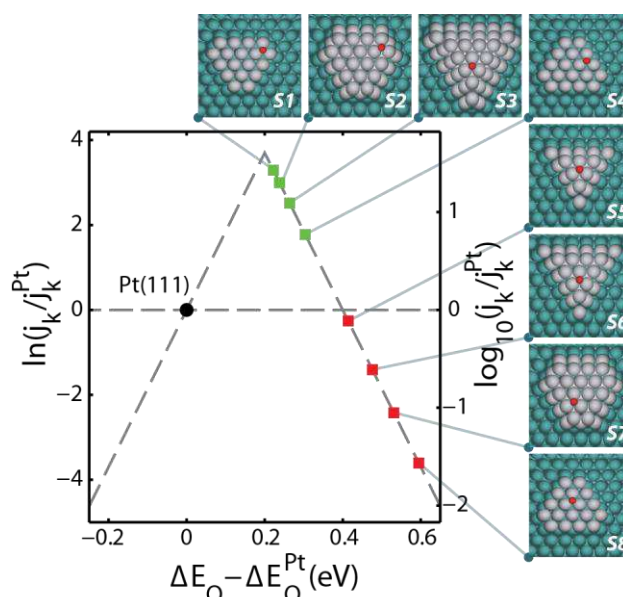
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Platinum is known to be among the best catalysts for oxygen reduction (ORR), though in recent years researchers have discovered that it binds oxygen too strongly for optimum activity [1]. Improvements have come by weakening the Pt-O adsorbate binding strength via alloying platinum with other transition metals such as Pt<sub>3</sub>Y [2] and Pt<sub>3</sub>Ni [3].

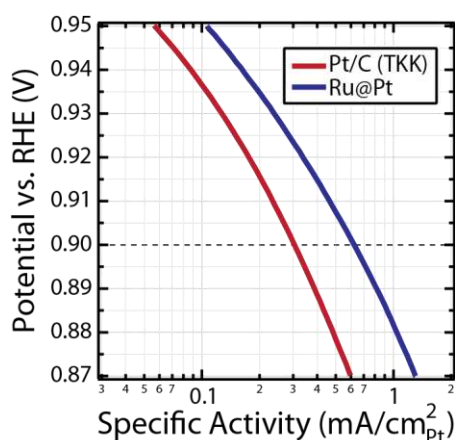
In this work, we suggest a strategy of tuning the adsorbate binding strength by tailoring core-shell nanostructures. To do this, two major effects are utilized: the over-weakening of binding for thin shell systems, and the strengthening of binding on undercoordinated sites found commonly on nanoparticles. It has been shown that single monolayers of platinum supported on various substrates can exhibit properties drastically different from platinum in its bulk form. In particular, one monolayer of platinum on ruthenium has been shown to have a much weaker Pt-O bond on the terrace (111) sites. However, by adding additional layers of platinum the effect is lessened and the O-Pt/Ru bond is strengthened [4,5]. Further significant strengthening of the binding will occur when moving from terrace sites to undercoordinated edge and corner sites which are prevalent in high surface area nanoparticulate catalysts.

Using density functional theory calculations, we identified the Ru@Pt core-shell system as a desirable candidate for an ORR electrocatalyst. To simulate a range of reaction sites that are likely to be present in real nanoparticles, we calculated the Pt-O binding energy on Pt clusters on a Ru substrate for a range of cluster sizes and adsorbate binding sites. Figure 1 shows these sites and plots their binding energy on the theoretical activity volcano.

Guided by the calculations, we have prepared Ru@Pt core-shell nanoparticles utilizing a liquid phase synthesis. Using a combination of STEM-EDS and Z-contrast (ADF-STEM) imaging, we confirm that the nanoparticles have the intended Ru-core, Pt-shell structure. Rotating disk electrochemistry was used to test catalytic activity. CO stripping was used to understand how Pt-shell thickness affects Pt-adsorbate bond strength. Optimally prepared samples exhibit increased ORR specific activity (Figure 2) by a factor of two compared to state of the art TKK platinum catalysts, 0.63 mA/cm<sup>2</sup><sub>Pt</sub> at 0.9V vs. RHE. This improvement is attributed to a weaker Pt-O bond, as evidenced by an anodic shift of ~35mV in the Pt-OH peak in the base cyclic voltammogram and weaker CO binding.



**Fig. 1** The ORR activity volcano with DFT calculated Pt-O binding energies for different sites of oxygen binding on clusters of Pt on Ru.



**Fig. 2** The specific activity of Ru@Pt compared with Pt/C (from TKK).

### References:

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