

## Insights on Oxygen Reduction Reaction on Au and Pt

### Polycrystalline Surface as Seen by *in situ* Surface

#### Enhanced IR Absorption Spectroscopy

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Unraveling detailed reaction pathways for oxygen reduction reaction (ORR) on metal surfaces has been a long-standing challenge in the field of electrocatalysis.<sup>1-2</sup> In this keynote presentation, we will discuss mechanistic insights on ORR on polycrystalline Au and Pt surface obtained by using *in situ* surface enhanced IR absorption spectroscopy (SEIRAS) that was further aided by *ab initio* DFT calculations in assigning observed reaction intermediates. With several reaction intermediates assigned, we were able to work out for the first time the ORR reaction pathways on Au in 0.1M HClO<sub>4</sub>, 0.1M H<sub>2</sub>SO<sub>4</sub>, and CF<sub>3</sub>SO<sub>3</sub>H supporting electrolytes. We will also discuss similar observations obtained on Pt surface. Proton transfer is likely the most important reaction-control step. Therefore, any mechanism that enhances proton transfer will probably enhance the ORR. Moreover, experimental evidence suggests that 3-fold ClO<sub>4</sub><sup>-</sup> adsorption helps stabilize hydronium on the surface and thus enhances the proton transfer reaction. In contrast, strong adsorption of HSO<sub>4</sub><sup>-</sup> seems to do the opposite.

1. Gewirth, A. A.; Thorum, M. S., Electroreduction of dioxygen for fuel-cell applications: materials and challenges. *Inorg. chem.* **2010**, *49*, 3557-3566.
2. Keith, J. A.; Jacob, T., Theoretical Studies of Potential-Dependent and Competing Mechanisms of the Electrocatalytic Oxygen Reduction Reaction on Pt(111). *Angew. Chem. Inter. Ed.* **2010**, *49*, 9521-9525.