

## Investigation of the Active Site of Rhodium Sulfide Electrocatalysts

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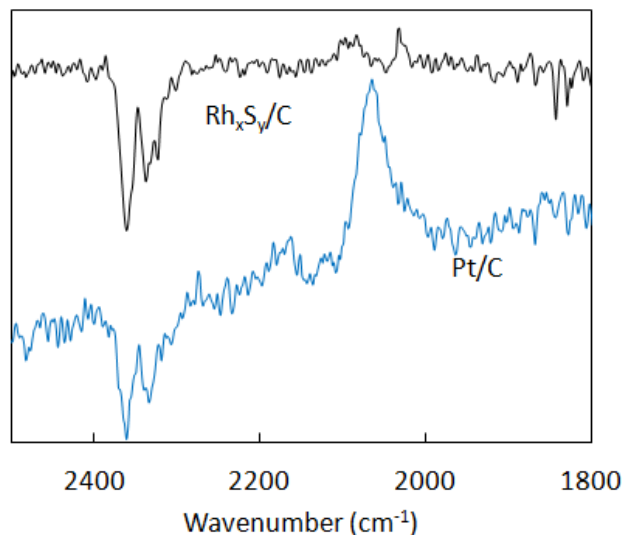
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Reliable, cost-effective, electrical energy storage is necessary for widespread adoption of time varying wind or solar resources. Although pumped hydroelectric and compressed air energy storage are the most commonly used technologies, there are a limited number of sites available and other means of energy storage are needed.

A H<sub>2</sub>/Br<sub>2</sub> proton membrane electrochemical flow battery is an option for large-scale energy storage because of its fast kinetics and high efficiency. The inherent advantage of flow cells over batteries is the decoupling of energy and power densities due to external storage of the active electrolyte.<sup>1,2</sup> For this type of flow cell, Rh<sub>x</sub>S<sub>y</sub>/C is the most active hydrogen electrocatalyst that is stable in HBr/Br<sub>2</sub>.<sup>3</sup> The active site for ORR of the mixed phase Rh<sub>x</sub>S<sub>y</sub> (Rh<sub>17</sub>S<sub>15</sub>, Rh<sub>2</sub>S<sub>3</sub> and Rh<sub>3</sub>S<sub>4</sub>) has been determined to be on the Rh<sub>3</sub>S<sub>4</sub> phase, specifically those involving Rh-Rh clusters through the use of Synchrotron-based X-ray absorption spectroscopy.<sup>4,5</sup> To determine the hydrogen evolution and hydrogen oxidation active sites we investigated the sensitivity of the catalysts to carbon monoxide poisoning. The carbon monoxide binding energies to the active sites were measured using temperature programmed desorption, hydrogen-deuterium exchange, electrochemical hydrogen evolution and oxidation, as well as Diffuse Reflectance Infrared Fourier Transform Spectroscopy. The observations were correlated to

calculations made, using density functional theory, of the binding energy of carbon monoxide on different active sites, to determine which sites may be contributing to the electrochemical activity.



**Figure 1.** Infrared spectroscopy showing carbon monoxide bound to rhodium sulfide and platinum.

### References:

1. G. H. Schuetz and P. J. Fiebelmann, *Int.J. of Hydrogen Energy*, **5**, 305 (1980).
2. R. S. Yeo and D.-T. Chin, *J. Electrochem. Soc.*, **127**, 549(1980).
3. A. Ivanovskaya et al., *Langmuir*, **29**, 480 (2013) 859.
4. J. M. Ziegelbauer et al., *J. Phys Chem. C*, **113**, 6955 (2009).
5. J. M. Ziegelbauer, D. Gatewood, S. Mukerjee, and D. E. Ramaker, *ECS Transactions*, **1**, 119 (2006).