

### Non-noble Metal Chalcogenides as Promising Candidates for Oxygen Reduction Reaction Catalysts in Fuel Cell Applications

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In anticipation of the coming hydrogen-based energy economy, a significant amount of work based on identifying cheaper and more practical materials for fuel cell catalysts is being performed world wide. While Pt and Pt alloys show by far the best activity for oxygen reduction reaction (ORR), it is limited by cost, availability and susceptibility to poisons such as those from the direct oxidation of methanol, chloride environments (Chlorine generation) and requirements for CO tolerance.

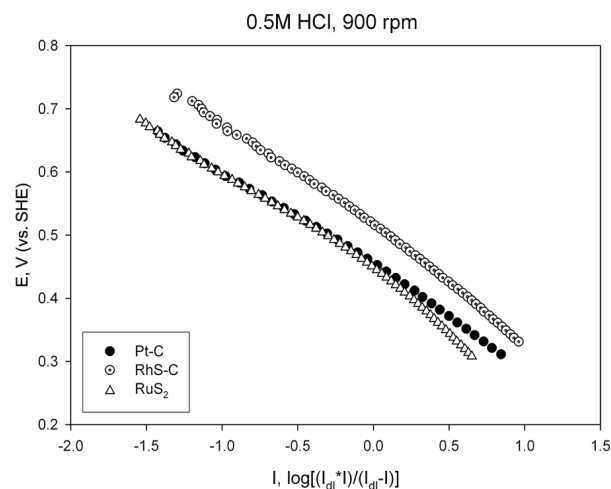
Transition metal-based chalcogenide complexes have been proposed as alternatives from not only the cost perspective, but also as an oxygen depolarized electrocatalyst for mitigation of poisoning from environments containing methanol and halide ions. [1-3] Prior reports, [4-6] on some chalcogenide complexes have demonstrated its vast superiority to platinum in such adverse environments. While a select few of these complexes have been exhaustively examined electrochemically and structurally, the reaction centers of a vast majority of these compounds are still disputed.[7-10] Therefore a significant window of opportunity exists for furthering materials development and our knowledge of structure property relationships in these complex compounds.

Figure 1 shows a representative plot comparing ORR reduction in 0.5 M HCl with  $RhS_x$  and  $RuS_2$ . A standard Pt/C (20% on Vulcan XC, 0.4 mg/cm<sup>2</sup>) was used as a control. As evident from the Tafel plots obtained,  $RhS_x$  exhibited better ORR activity than Pt, while the  $RuS_2$  performance was close to the control.

In this work, a variety of promising candidates are examined. The materials were synthesized from metal carbonyl and chloride precursors.[11, 12] Rotating ring disk electrode measurements were performed in a variety of electrolytes to examine the activities and kinetics of these complexes in comparison to platinum. Structural characterizations were performed via XRD and SEM (EDAX). In addition, preliminary *in situ* and *ex situ* EXAFS and XANES data will be presented. The synchrotron based *in situ* XAS spectroscopy will also be used to elucidate the element specific corrosion characteristics of these compounds.

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**Figure 1:** Mass transfer-corrected Tafel plots from glassy carbon RRDE studies of three ORR catalysts in oxygen-saturated 0.5M HCl at 900 rpm, scan rate 20 mV s<sup>-1</sup>. 20% platinum on Vulcan XC72 (E-TEK), 30% RhS on Vulcan XC72, and unsupported  $RuS_2$  thin films.

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