



Investigation of the Electrocatalytic Activity of Rhodium Sulfide for Hydrogen Evolution and Hydrogen Oxidation



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ABSTRACT

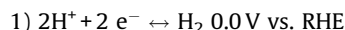
We report the synthesis of unsupported and carbon-supported, mixed phase, rhodium sulfide, using both a hydrogen sulfide source and a solid sulfur source. Samples with several different distributions of rhodium sulfide phases (Rh_2S_3 , $\text{Rh}_{17}\text{S}_{15}$, RhS_2 and metallic Rh) were obtained by varying the temperature and exposure time to H_2S or sulfur to rhodium ratio when using solid sulfur. Samples were characterized by X-ray diffraction (XRD), and the unsupported rhodium sulfide compounds studied using Raman spectroscopy to link Raman spectra to catalyst phases. The electrocatalytic activity of the rhodium sulfide compounds for hydrogen evolution and oxidation was measured using rotating disk electrode measurements in acidic conditions to simulate use in a flow cell. The most active phases for hydrogen evolution were found to be Rh_3S_4 and $\text{Rh}_{17}\text{S}_{15}$ (-0.34 V vs. Ag/AgCl required for 20 mA/cm^2), while Rh_2S_3 and RhS_2 phases were relatively inactive (-0.46 V vs. Ag/AgCl required for 20 mA/cm^2 using RhS_2/C). The hydrogen oxidation activity of all rhodium sulfide phases is significantly lower than the hydrogen evolution activity and is not associated with conductivity limitations.

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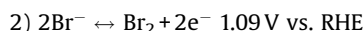
1. Introduction

Cost-effective electrical energy storage is important for matching power production to power utilization and to optimize the use of time varying renewable resources. Flow batteries have the potential to be among the lowest cost alternatives [1,2]. The H_2 - Br_2 flow battery has the advantages of lower overpotentials than many other flow cell systems, a high power density, a high energy density, and relatively high reliability [3–5].

The H_2 - Br_2 cell consists of a hydrogen half reaction:



and a bromine half reaction:



A proton-conducting membrane separates the hydrogen electrode from the bromine electrode and allows transport of the protons involved in the hydrogen reaction. The bromine electrode reaction proceeds rapidly on carbon without a metal

catalyst [5,6]. The hydrogen electrode reactions, however, require a catalyst for the hydrogen evolution reaction (HER) during charge and the hydrogen oxidation reaction (HOR) during discharge. For the H_2 - Br_2 cell, the hydrogen electrocatalyst must be stable in the presence of bromide and bromine. Nanoparticulate metals such as platinum supported on carbon, though initially active [7,8], are subject to corrosion or deactivation due to bromine/bromide crossover through the membrane [6].

Metal sulfides supported on carbon including rhodium sulfide ($\text{Rh}_x\text{S}_y/\text{C}$), are used commercially as oxygen depolarized cathodes in HCl [9–13]. These materials are also active as HER/HOR catalysts and are more stable than Pt/C, even in the corrosive HBr/Br_2 electrolyte [6,14,15]. However, the activity for HOR of rhodium sulfide is low compared to the activity for HER, even in the absence of bromide ions [6,14], unlike platinum, which is equally active for both hydrogen evolution and oxidation, until bromide/bromine crossover occurs [6]. For the H_2 - Br_2 flow cell to operate reliably at high efficiency, the HOR activity of the stable $\text{Rh}_x\text{S}_y/\text{C}$ must be understood and improved.

One possible explanation for the low HOR activity of the multi-phase rhodium sulfide is its conductivity. Semiconductor electrodes in the absence of illumination can be poor bi-directional conductors due to the lack of mobile charge carriers. For example,

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an n-type semiconductor (such as RuS_2) may be capable of reduction reactions under forward bias, but hindered for oxidation reactions under reverse bias [16,17]. The rhodium sulfide catalyst consists of several phases ($\text{Rh}_{17}\text{S}_{15}$, Rh_2S_3 and Rh_3S_4) [10], with $\text{Rh}_{17}\text{S}_{15}$ and Rh_3S_4 being reported as conducting semi-metals [18,19], and Rh_2S_3 reported as a true semiconductor [10,20–23]. The low hydrogen oxidation activity of the $\text{Rh}_x\text{S}_y/\text{C}$ catalyst may therefore be due to the semiconducting properties of the Rh_2S_3 phase.

It should be possible to determine which phases contribute to the HER activity and what limits the HOR activity by isolating the rhodium sulfide phases both with and without a carbon support. For the oxygen reduction reaction in HCl on the $\text{Rh}_x\text{S}_y/\text{C}$ catalyst, the Rh_3S_4 phase is believed to be the active phase, based on local structure analysis using X-ray absorption spectroscopy [9,10]. For the $\text{Rh}_x\text{S}_y/\text{C}$ catalyst, it is thought that the Rh_3S_4 and Rh_2S_3 are amorphous, but present in the catalyst, making them difficult to characterize by X-ray diffraction [24]. Determination of the most active distribution of phases within a catalyst is not straightforward, as an intermediate mixture of $\text{Rh}_{17}\text{S}_{15}$ –Rh was found to be most active for ORR [25].

Alternative routes exist to synthesize unsupported, crystalline Rh_2S_3 [26]. Depending upon the annealing conditions, Rh_2S_3 can be converted to the other phases by loss of sulfur [18]. Rh_3S_4 can also be synthesized and characterized by X-ray diffraction [27,28], but $\text{Rh}_{17}\text{S}_{15}$ is still present in the mixture [19]. The phases formed are dependent on the temperature and stoichiometry of the sulfur and rhodium [19,27,28]. At a temperature of 1100 °C Rh_3S_4 or Rh_2S_3 , may result depending on the stoichiometry of the rhodium and sulfur [27].

We are interested in understanding the relationship of the electrocatalytic activity of rhodium sulfide to the phases present in the catalysts. By synthesizing rhodium sulfide electrodes with different phases, their contributions to the hydrogen evolution activity can be determined. Further, with unsupported electrocatalysts the conductivity and photoconductivity of the semiconducting phases can be assessed. The unsupported electrodes can also be used for spectroscopic measurements such as Raman, without the confounding effects of the carbon support. This understanding of which phase is active will enable us to specifically synthesize more active catalyst phases while minimizing rhodium use. Further we hope this, with the help of theory will lead to understanding why hydrogen oxidation is not as active as hydrogen evolution. In this communication we address the following specific questions: 1) How can synthesis conditions (precursor, temperature, time, and ramp rate) be used to control the final phases of Rh_xS_y unsupported and supported on carbon? 2) What is the relation of Rh_xS_y phases to the activity of HER and HOR? 3) How does charge transfer conductivity of the Rh_xS_y phases compare to metallic catalysts, and does it limit the HOR activity?

2. Experimental

2.1. Carbon supported catalysts synthesis.

Pt/C was purchased from ETEK. Commercial $\text{Rh}_x\text{S}_y/\text{C}$ was obtained from BASF. The commercial catalyst is synthesized by the addition of thio-containing compounds to a solution of rhodium salt, followed by heat treating. For the rhodium sulfide compounds on carbon synthesized in this work the sulfur source was H_2S , similar to that used for other metal sulfides [14,24], with the advantage of lower temperatures and thus potentially lower particle sizes [24]. The rhodium sulfide on carbon samples were synthesized by adding a 1 M solution of RhCl_3 or $\text{Rh}(\text{NO}_3)_3$ to XC72 carbon then drying at 110 °C in air for one hour. The loading was selected to make 30 wt% metal. The dried precursor on carbon

was heated in Ar or in 1:1 $\text{N}_2:\text{H}_2\text{S}$, and held at a given temperature in 1:1 $\text{N}_2:\text{H}_2\text{S}$ before cooling (again either in Ar or in H_2S depending on the synthesis recipe). Conditions such as the ramp rate during heating, temperature, and time at maximum temperature were varied in an attempt to modify the final product. Certain samples were post-treated by annealing in argon.

2.2. Unsupported catalysts synthesis by hydrogen sulfide.

Hydrogen sulfide was reacted with a $\text{Rh}(\text{NO}_3)_3$ precursor in crucibles in a similar manner as the carbon supported catalysts. $\text{Rh}(\text{NO}_3)_3$ was used instead of rhodium chloride because it was easier to work with as a precursor when weighing out appropriate amounts of the rhodium due to the hygroscopic nature of the salt. Unsupported catalysts were also prepared using elemental sulfur by combining Rh, RhCl_3 or Rh/RhCl_3 and S in a quartz ampoule that was evacuated to 10^{-4} Torr and then heated to temperatures ranging from 1035–1100 °C for 2 days. This method has previously been used to form Rh_3S_4 , as well as Rh_2S_3 and $\text{Rh}_{17}\text{S}_{15}$ [19].

2.3. X-Ray Diffraction and Electron Microscopy.

X-ray diffraction (XRD) data was collected on a PANalytical, Inc. X'Pert powder diffractometer using a $\text{Cu K}\alpha$ source (1.54 Å photon wavelength). Rietveld refinements to find the weight fraction of the crystalline phase were done using PyGSAS [29]. CIF files for Rh_2S_3 , $\text{Rh}_{17}\text{S}_{15}$, Rh, RhS_2 and Rh_3S_4 were used for the refinement. Transmission electron micrographs of the catalyst were obtained using a TEM FEI T20-EDX.

2.4. Preparation of electrocatalyst inks and electrodes.

Inks of the electrocatalysts were synthesized by mixing 6 mg of the catalyst with 1 mL of 1:1 isopropanol:water, with 32 μL of a 5 wt% Nafion solution. This solution was ultrasonicated for 24 hours before use. The catalyst on carbon were synthesized at a slightly lower concentration, using 3 mg of catalyst on carbon with 5 mL of 1:1 isopropanol:water with 16 μL of a 5 wt% Nafion solution. Electrodes were prepared by depositing the ultrasonicated ink on a glassy carbon disk in a rotating disk electrode in 8 μL aliquots (for a total of 16 μL) and drying at 100 °C.

2.5. Hydrogen evolution and oxidation activity.

The HER activity of the electrocatalyst was measured by conducting a cyclic voltammogram in 1 M H_2SO_4 using a Pt counter electrode, a Ag/AgCl reference electrode, and a VSP Bio-Logic potentiostat. A Pine Instruments rotating disk electrode was used with 1500 rpm rotation rate. IR compensation was done with EC-Lab software (PEIS). The HOR activity was measured after bubbling hydrogen into 1 M H_2SO_4 solution while rotating at specified speed until the open circuit voltage reached a constant value, then conducting a linear sweep voltammogram. The photoresponse of the unsupported catalysts was measured by turning on and off illumination from a Cuda Products white-light solar simulator halogen lamp to the catalyst and measuring the current response.

2.6. Double layer capacitance for surface area normalization.

Double layer capacitance was assumed to be proportional to the surface area of the catalyst-electrolyte interface. This surface area was used to normalize the hydrogen evolution currents of the unsupported electrodes. The capacitance was measured by conducting cyclic voltammetry in 1.0 M H_2SO_4 in the region of 0.4 to 0.6 V vs. Ag/AgCl at different scan rates (1000 to 20 mV/s).

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