



Tuning the activity/stability balance of anion doped $\text{CoS}_x\text{Se}_{2-x}$ dichalcogenides

Y. Li^a, T. Polakovic^b, J. Curtis^b, S.L. Shumlas^c, S. Chatterjee^a, S. Intikhab^a, D.A. Chareev^{d,e,h}, O.S. Volkova^{d,f,g}, A.N. Vasiliev^{d,f,g}, G. Karapetrov^b, J. Snyder^{a,*}

^a Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States

^b Department of Physics, Drexel University, Philadelphia, PA 19104, United States

^c Department of Chemistry, Temple University, Philadelphia, PA 19122, United States

^d Ural Federal University, 620002 Ekaterinburg, Russia

^e Institute of Experimental Mineralogy, RAS, 142432 Chernogolovka, Russia

^f Low Temperature Physics and Superconductivity Department, Physics Faculty, M. V. Lomonosov Moscow State University, Moscow 119991, Russia

^g National University of Science and Technology MISiS, Moscow 119049, Russia

^h Institute of Geology and Petroleum Technologies, Kazan Federal University, Kazan, Russia

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ABSTRACT

We present a thorough assessment of the compositional dependent hydrogen evolution reaction (HER) activity and stability for Co-based mixed chalcogen, $\text{CoS}_x\text{Se}_{2-x}$, transition metal dichalcogenides (TMDs). In direct contrast to other reports on mixed chalcogen TMDs that have been limited to Mo and W, we observe a decrease in HER activity for any departure from the pure, single chalcogen composition, CoS_2 and CoSe_2 . The single chalcogen TMDs are found to have nearly identical HER activity. Bulk resistivity of the pure and mixed chalcogen TMDs as well as the charge transfer resistance for the HER are found to be most optimal for CoSe_2 . However, CoSe_2 is predicted to have an endothermic hydrogen adsorption free energy in contrast to the slightly exothermic hydrogen adsorption free energy for CoS_2 . This highlights the convolution of hydrogen adsorption free energy and material conductivity in determining the HER activity for even metallic conducting TMDs. Sulfur-rich Co-based TMDs with a pyrite-type crystal structure are found to quickly deactivate through loss of Co and formation of passivating reduced sulfur species at the surface while Se-rich compositions are observed to be more stable. Therefore, with an HER activity matching that of CoS_2 , but with a dramatic improvement in stability, CoSe_2 breaks away from the traditional inverse activity – stability relationship and represents a promising non-PGM HER electrocatalyst for acidic PEM electrolyzers.

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1. Introduction

The future of renewable energy centers on the advancement of technologies that will bridge the gap between peak energy production and peak energy demand as well as readily make the transition from stationary to portable power. Storing the energy produced from intermittent renewable sources in the form of chemical bonds shows great promise for both stationary and transportation applications. Hydrogen represents one of the simplest forms of electrochemical fuels. With a high gravimetric energy density (120 MJ/kg) [1] and sourced from water, hydrogen is an ideal energy storage fuel, operating outside of the carbon cycle. Polymer electrolyte membrane (PEM) electrolysis is an advanced,

commercialized technology for the generation of H_2 from H_2O ; however, both the cathode (H_2 side) and anode (O_2 side) electrodes are loaded with precious metal based catalysts, typically Pt on the cathode and Ru and/or Ir oxides on the anode [2–4]. The expense and limited availability of these catalytic materials puts a significant constraint on the wide-spread adoption of electrochemical fuel generation technologies. The task then becomes finding an earth-abundant material that has comparable activity and stability to the requisite precious metal based catalysts.

Sulfur-based transition metal dichalcogenides (TMDs) have emerged as a promising alternative to platinum group metal (PGM) hydrogen evolution reaction (HER) electrocatalysts as they are abundant, inexpensive, and exhibit a low HER overpotential with surprising stability in acidic electrolytes, $\text{pH} \leq 1$ [5–13]. Naturally occurring enzymes including hydrogenases and nitrogenases efficiently split water at sulfur coordinated Mo and Ni/Fe

* Corresponding author.

E-mail address: jds43@drexel.edu (J. Snyder).

metal centers [13,14]. TMDs closely mimic the active site geometry and coordination structure of these enzymes with molybdenum disulfide (MoS_2), a common hydrodesulfurization catalyst [7,12,15], emerging as the standard for TMD HER electrocatalysts [5,6,8,9,12,15–26]. Initial studies of well-defined MoS_2 thin films identified the edges as active sites while the basal planes were determined to be inactive [12]. Subsequent computational analysis of the HER reaction on two-dimensional TMDs has quantified the adsorption free energy of atomic hydrogen (ΔG_{Had}) on different edge/basal structures and compositions, corroborating the experimental results while giving important insight for further optimization [9,12,15,20,22,24,25,27]. The adsorbed hydrogen intermediate is found to have the most optimal ΔG_{Had} , closest to thermoneutral, at the S-edge of the MoS_2 2D structure [15,20,22,28]. The edges of 2D MoS_2 are also found to have metallic electronic character [7,8,12,15,17,19,24,29], while MoS_2 itself is a semiconducting material [12,21,29]. The HER overpotential for bulk MoS_2 is prohibitively high and only after directed nanostructuring of MoS_2 to preferentially expose the active edge sites is an appreciable activity obtained [5,6,9,12,18,19,21,30,31].

Since the first reports of the high intrinsic activity of the edge sites of 2D MoS_2 [12], significant effort has been centered on optimizing nanoscale geometry to expose the highest density of edge sites and maximize activity [5,6,9,16–19,21,32–35]. Further optimization of TMD HER activity has been achieved through the addition of transition metal (cation) dopants into the TMD lattice [20,25,31]. Transition metal dopant species incorporated in the edge of MoS_2 were found to shift the ΔG_{Had} on both the Mo-edge and S-edge. The S-edge of the doped TMDs is predicted to exhibit similar HER activity to the Mo-edge of undoped TMDs [20,25]. For single metal 2D TMDs, the hydrogen adsorption strength is calculated to be prohibitively weak on the S-edge. As the S-edge makes up nearly half of the exposed surface in 2D TMDs [20], an optimization of the H-binding on the S-edge effectively increases the active site density and thus the catalytic activity. For many TMDs, the impact of doping with a second chalcogen (anion) on the electronic structure is found to be small in comparison to cation doping [7,6]. However, in seeming contradiction to the theoretical calculations relying on ΔG_{Had} as the singular activity descriptor, recent work assessing the impact of anion doping, either in the form of $\text{MS}_{(x)}\text{X}_{(2-x)}$ [36,37] ($X = \text{Se}, \text{Te}$) or through heterostructures with a high interfacial area between MS_2 and MX_2 rich phases [38,39], have demonstrated significant improvements in the HER activity. These observed HER activity enhancements have been noted for W [38] and Mo [36,37] based TMDs where in each case the highest activity was found for the mixed chalcogen compositions. The origin of this activity enhancement has been attributed to several potential sources: (1) the introduction of a second chalcogen atom into the TMD lattice causes a strain at the surface, modifying the geometric and electronic structure and optimizing ΔG_{Had} ; (2) evolution of a high interfacial area between MS_2 -rich and MX_2 -rich phases through phase separation, optimizing ΔG_{Had} ; or (3) anion doping induced changes to the TMD atomic geometry, shifting it from semiconducting, which is the dominant electronic behavior of both MoX_2 and WX_2 [5,8,9,12,15,17,18,40], to metallic and thus improving the charge transfer through the catalyst.

While only the low-coordinated sulfur atoms on the Mo-edge of exfoliated 2D- MoS_2 are active for the HER due to the low conductivity and weak adsorption of atomic hydrogen on the basal planes, pyrite-group TMDs, including CoS_2 and CoSe_2 , are HER active in their bulk form due to their intrinsic metallic-like conductivity [11,13,30,40–44]. The $\text{CoS}_x\text{Se}_{2-x}$ pyrite-type cubic crystal structure (No. 205, $T_h^6, Pa\bar{3}$) is closely related to that of NaCl (No. 225, $O_h^5, Fm\bar{3}m$), with Co atoms at the face-centered positions of Na sites

and centers of S_2/Se_2 dumbbells at the Cl sites. These dumbbells are oriented along the $(1\ 1\ 1)$ directions in the unit cell, with each unit cell containing four $\text{CoS}_2(\text{Se}_2)$ molecules. Each Co atom is surrounded by six chalcogen atoms forming a trigonally distorted octahedron, where each chalcogen links to three Co atoms and a single other chalcogen atom, forming a distorted tetrahedral structure [45]. The octahedral crystal field at each Co atomic site splits the degenerate Co-3d band into e_g and t_{2g} sub-bands. The Co- t_{2g} band is lower in energy and is completely filled with six electrons, while the Co- e_g band has one electron per Co atom. Since the narrow Co- e_g band crosses the Fermi surface, any electronic properties of the material are being dominated by the structure of the Co- e_g band and correlations of the electrons in this band. The electronic properties of doped Co chalcogenides, CoS_2 and CoSe_2 , are directly tied to the degree of interaction between the Co- e_g orbitals and the chalcogen's p orbitals. The Co- e_g orbitals expand along the axis towards the chalcogen atoms and hybridize with the antibonding p^* orbitals arising from chalcogen pairs (specifically from the S-3p or Se-4p) [46], increasing the e_g bandwidth [47]. Calculations indicate that although the lattice constant increases by $\sim 5\%$ when increasing Se content in $\text{CoS}_x\text{Se}_{2-x}$, the hybridization is stronger between the e_g and p^* states in CoSe_2 than in CoS_2 [48,49], therefore the bandwidth increase of Co- e_g sub-band correlates with increase of Se concentration in $\text{CoS}_x\text{Se}_{2-x}$. The slightly increased density of states at the Fermi level in CoSe_2 compared to CoS_2 results in higher conductivity (by a factor of two) in the former at room temperature [50]. The width of the Co-3d band is determined by the degree of hybridization with the anti-bonding dichalcogen p^* band. As the hybridization is stronger in the CoSe_2 case, a continuous decrease in Co-3d bandwidth is expected with decreasing Se concentration in $\text{CoS}_x\text{Se}_{2-x}$. This change in the d-band bandwidth could have an effect on electrocatalytic processes. Density Functional Theory (DFT) calculated ΔG_{Had} values indicate that CoS_2 is expected to bind H slightly too strong (-0.08 eV, exothermic adsorption) whereas CoSe_2 is expected to bind H too weakly (0.49 eV, endothermic adsorption) [24]. Considering ΔG_{Had} as the singular activity descriptor, an intuitive strategy for pushing toward zero HER overpotential on non-PGM TMDs is the manipulation of the electronic structure of Co-based pyrite-group TMDs through controlled chalcogen (anion) doping. It is expected that the addition of small amounts of Se to CoS_2 , creating a mixed chalcogen TMD, will bring the doped TMD closer to thermoneutral ΔG_{Had} , increasing HER activity. While the HER activities of CoS_2 and CoSe_2 have been shown to be competitive, CoS_2 demonstrates a significant degree of instability in terms of both material and activity loss during potential cycling and extended HER electrolysis [11,13,30,40–44]. The low HER overpotential, for a non-PGM catalyst, and observed instability places CoS_2 in a familiar class of electrocatalytic materials that are characterized by an inverse relationship between activity and stability [2,3,10,51,52]. CoSe_2 , however, is found to exhibit a higher degree of stability at cathodic potentials [53]. In addition to the manipulation of ΔG_{Had} , it may also be possible to obtain a balance between activity and stability through chalcogen doping of CoS_2 and CoSe_2 TMDs.

In this study, we use chalcogen (anion) doped $\text{CoS}_x\text{Se}_{2-x}$ to assess their impact on the balance between HER activity and material stability. Through potentiodynamic polarization and constant potential electrolysis, we assess the HER activity and discuss the observed trends with regards to standard activity descriptors, hydrogen adsorption free energy (ΔG_{Had}). Additionally, we highlight the importance of material properties beyond the singular activity descriptors, specifically bulk resistivity/conductivity. Finally, we assess the compositional dependent operational stability of the pure and chalcogen (anion) doped TMDs through

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