

# Study on the active sulfur site of thiomolybdate clusters on carbon nanotubes for hydrogen evolution reaction

*Han-Ik Joh<sup>1</sup>, and Sungho Lee<sup>2,\*</sup>*

*<sup>1</sup>Department of Energy Engineering, Konkuk University, Seoul, Republic of Korea*

*<sup>2</sup>Carbon Convergence Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Jeollabukdo, Republic of Korea*

## **Abstract**

Hydrogen has been one of the most promising energy enable to innovatively alter the current fossil fuel system that have induced energy and environmental crisis. In order to produce hydrogen through the environmentally friendly pathway, highly active and cost-effective catalysts for electrolysis of water should be developed. Among the various kinds of alternatives for the highest active platinum catalysts, molybdenum sulfides based electrocatalysts exhibited an excellent hydrogen evolution reaction (HER) activity and stability due to the low Gibbs energy at edge sites of molybdenum sulfides. However, unlike the edges, the basal plane of the molybdenum sulfides has an inert for the HER. [1-3] Hence, the active sites of molybdenum sulfides should be effectively enlarged to realize the practical catalysts.

Recently, thiomolybdate clusters, which are composed by few molybdenum and sulfur atoms such as  $[\text{Mo}_3\text{S}_{13}]^{2-}$  and  $[\text{Mo}_2\text{S}_{12}]^{2-}$ , were introduced as one of the most efficient catalysts. They could use not only edge sites but entire surfaces of the cluster for the HER because of intrinsically exposed sulfurs. However, the origin of the active sites among the three kinds of sulfur bonding, such as terminal S, bridge S, and apical S, have been still unknown.

In this study, we introduce a facile transition way from amorphous  $\text{MoS}_3$  to the  $[\text{Mo}_3\text{S}_{13}]^{2-}$  clusters using additional supply of sulfur sources and synthesize highly active and reliable clusters on commercial multiwalled carbon nanotubes. The designated electrocatalyst,  $[\text{Mo}_3\text{S}_{13}]^{2-}/\text{MWCNT}$ , showed excellent electrochemical HER activity with onset potential of  $\sim 100$  mV, Tafel slope of  $\sim 40$  mV/decade, and stability for 1,000 cycles with  $\sim 5\%$  decay. In addition, through the selective low temperature treatment, we tried to identify the active sulfur bonding. It was observed that the electrocatalytic activity of the catalyst was significantly decreased when the bridge sulfur in the cluster was selectively removed. Therefore, we believed that

bridge and apical sulfurs were important roles to realize the highly active and stable catalysts [4].

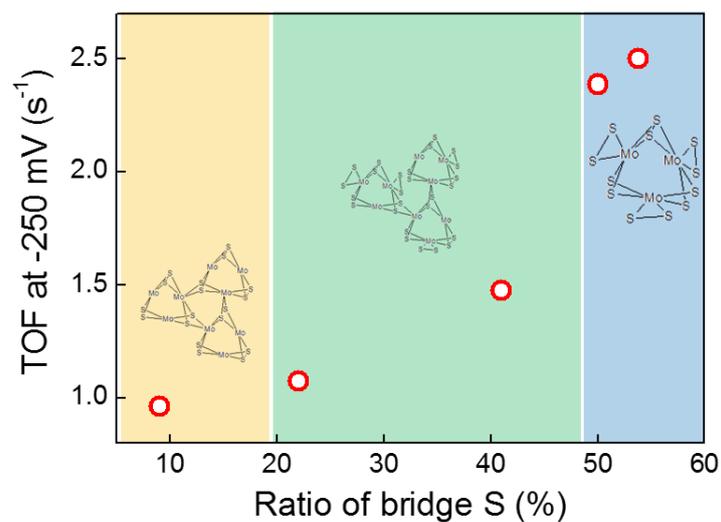


Figure. Turnover frequency at 250 mV as a function of ratio of bridge sulfur

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