Influence of various types of additives on molybdenum disulfide electrocatalytic activity for hydrogen evolution

Jelena Rmuš Mravik[1], Milica Pejčić[2], Željko Mravik[1], Blaž Belec[3], Milica Prvulović[1], Ivana Stojković Simatović[4], Sandra Kurko[1]
[1]*Center of excellence for hydrogen and renewable energy (CONVINCE), Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia*
[2]*Vinča Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Belgrade, Serbia*
[3]*Materials Research Laboratory, University of Nova Gorica, Ajdovščina, Slovenia*
[3]*Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia*

Molybdenum disulfide (MoS_2), as a typical transition metal dichalcogenide, has shown promising catalytic activity for hydrogen evolution reaction (HER) due to its layered structure with a large number of active sites. MoS_2 structure consists of several layers connected with weak Van der Waals attraction between them, while strong covalent bonds are within the layer. Due to this structure, MoS_2 exhibits distinct surface sites and significantly faster electron and hole mobility along the basal plane than perpendicularly between the layers [1]. Different nanostructured forms showed a variety of catalytically active sites such as plane edges, defects in the structure (vacancies, dislocations, dopant atoms), or unsaturated bonds. The layered structure of MoS_2 is easily modified to obtain a large number of active sites for HER. The main drawbacks are a lack in conductivity and a basal plane that is catalytically inert. Consequently, the performance of the material is largely limited by its conductivity and concentration of available active sites. Therefore, different strategies are employed in order to increase charge transport and create more active sites in the material. Mechanochemical modification of the material can cause a decrease in the size of the particles, *i.e.* increase in specific surface area, creation of structural changes (formation of defects and displacement of atoms, splitting of layers), amorphization, etc. The changes that the mechanochemical modification will cause in the material depend on the different milling parameters, among which is the milling time. The additional incorporation of conductive additives can be further beneficial for the catalytic activity of MoS_2. MoS_2 composites with different conductive materials can be easily prepared using mechanochemical milling. This method is shown to be very suitable for the preparation of composites - apart from homogenization, it also leads to morphological changes and the creation of defects, which is favourable for HER [2].

In this work, to improve the electrical conductivity of electrocatalysts, composites of MoS_2 with graphene oxide or bismuth selenide are prepared. Graphene oxide is a carbon nanomaterial that has high specific surface area, adjustable surface chemistry and electronic properties [3], which makes it suitable for the synthesis of composites with MoS_2. Bismuth selenide is a topological insulator, a material that is an insulator in the bulk but possesses metallic surface states [4] and therefore are expected to be good conducting channel for electron transport. Therefore, combining such materials with the catalytic active but poorly conductive MoS_2 could result in enhanced electron transfer and improved HER activity of the material.

The molybdenum disulfide and bismuth selenide were obtained by hydrothermal synthesis, while graphene oxide was prepared by the modified Hummers' method. Thus, prepared constituents are combined in different mass ratios and milled using a high-energy ball mill (SPEX Mixer/Mill 5100). The obtained composites were studied as catalysts for hydrogen evolution reaction in an acidic solution. SEM images of prepared composites showed that constituents are homogeneously mixed and cannot be distinguished separately. XRD analysis showed that bismuth selenide remained unchanged after the milling of composites, while graphene oxide undergoes some amorphization. These changes lead to different catalytic behavior of composites, depending on the type of additives. Therefore, composites with bismuth selenide exhibit significantly better catalytic activity for HER than composites with graphene oxide under the same conditions.

Acknowledgement: This research was financially supported by the Serbia-Slovenia bilateral project No.337-00-21/2020-09/39, the Slovenian Research Agency through the research core funding no. P2-041 and NATO SPS G6037. Authors acknowledge support from Ministry of Science, Technological Development and Innovation of the Republic of Serbia under contract 451-03-66/2024-03/200017.

References

1. J. D. Benck *et al.*, *ACS Catalysis*, **4** (2014), 3957-3971. https://doi.org/10.1021/cs500923c
2. J. Rmuš *et al.*, *J. Energy Storage*, **68** (2023), 107719. https://doi.org/10.1016/j.est.2023.107719
3. Z. Jovanović *et al.*, *Electrochim. Acta*. **258** (2017) 1228–1243. https://doi.org/10.1016/j.electacta.2017.11.178
4. B. Belec *et al.*, *Scientific reports*, **9** (2019), 19057. https://doi.org/10.1038/s41598-019-55646-1