Metal-Doped Catalysts for Hydrogen Evolution Reaction

Tucker Morey  
*Pittsburg State University*

Ram K. Gupta  
*Pittsburg State University*

Pawan K. Kahol  
*Pittsburg State University*

Follow this and additional works at: [https://digitalcommons.pittstate.edu/posters_2019](https://digitalcommons.pittstate.edu/posters_2019)

Recommended Citation
[https://digitalcommons.pittstate.edu/posters_2019/43](https://digitalcommons.pittstate.edu/posters_2019/43)

This Article is brought to you for free and open access by the Research Colloquium 2019 at Pittsburg State University Digital Commons. It has been accepted for inclusion in Posters by an authorized administrator of Pittsburg State University Digital Commons. For more information, please contact dlwhite@pittstate.edu.
Metal Doped Catalysts for Hydrogen Evolution Reaction

Tucker Morey, Pawan K. Kahol, and Ram K. Gupta
Pittsburg State University, Pittsburg, Kansas

Background and Purpose

- The rapid depletion of fossil fuels and growing environmental concerns have created an enormous worldwide demand for alternative clean energy technologies.
- Hydrogen has a potential to be one of the most effective clean energy sources due to its high energy density of 141.86 MJ/kg and clean combustion.
- Water electrolysis via photochemical and photoelectrochemical are the promising pathways for sustainable hydrogen production.
- The water splitting reaction can be expressed chemically as:
  \[
  \text{Total reaction } 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \ (1.23\text{V})
  \]

Materials and Methods

- Ammonium heptamolybdate was dissolved in water followed by the introduction of the transition metal precursor.
- The molar ratio of M to Mo was 2%.
- Aniline was added dropwise followed by 1M HCl to adjust the pH between 2 and 4.
- The solution was heated in an oil bath to 50°C for 4 hours, washed with ethanol and water, then dried overnight at 50°C.
- Carburized samples occurred in a fixed-bed quartz micro-reactor at 800°C for 5 hours in an argon atmosphere.
- During the cool-down process, the samples were passivated in 1% \( \text{O}_2/\text{Ar} \) for 12 hours.
- Final products were denoted as 2% \( \text{M-Mo}_x\text{C} \) (M: Fe, Co, Ni, Cu, Ag, and Pt).
- For comparison, the commercial HER catalyst 20% Pt/C was employed.
- Samples were loaded on glassy carbon electrode of 3 mm diameter.
- All electrochemical tests performed in 0.5M \( \text{H}_2\text{SO}_4 \).
- All potentials are reported with reference to reversible hydrogen electrode + (0.198 + 0.059 pH) V.

Results

- X-ray diffraction peaks at 20 of 34.8°, 38.4°, 39.8°, 52.5°, 61.9°, 69.6° and 74.9° are associated with \( \beta\)-\( \text{Mo}_x\text{C} \). Fe, Co, and Ag doped \( \text{Mo}_x\text{C} \) displayed an additional peak at 20 of 40.5°, indicative of metallic Mo. The peak at 20 of 39.8° shifted to lower diffraction angles from the replacement of metal atoms.
- Mo 3d X-ray photoelectron spectroscopy for Ni, Cu, and Pt doped \( \text{Mo}_x\text{C} \) displayed 4 Mo species. Peaks with binding energy of 228.0-228.6 eV is from Mo\(^{3+}\) in Mo-C bonding. Mo\(^{4+}\) binding energy lowered when metal doped indicate enriched electron density. Metallic Mo was detected for Fe, Co, and Ag doped \( \text{Mo}_x\text{C} \).
- Brunauer-Emmett-Teller analysis provided sharp decrease in surface area when doped with Fe or Co along with increased average pore size, while the Pt doped \( \text{Mo}_x\text{C} \) displayed a drastically increased surface area and decreased pore size.
- Scanning transmission electron microscopy showed that Fe doped \( \text{Mo}_x\text{C} \) had a random morphology while all other metal doped \( \text{Mo}_2\text{C} \)s were wire-like morphologies (diameter of 50-100 nm) composed of nanoparticles of 3-10 nm. There are small (100-200 nm) nanoparticles attacked on the \( \text{Mo}_2\text{C} \) wire surface.
- Polarization curves show that 2% Pt-\( \text{Mo}_x\text{C} \) had an overpotential of 79 mV and onset potential of 32 mV compared to the commercial 20% Pt/C overpotential of 34 mV and onset potential of 23 mV.

Conclusions

- The molybdenum oxides Mo\(^{3+}\) (MoO\(_2\)), Mo\(^{4+}\) (\( \text{MoO}_2 \_\text{C} \)), and Mo\(^{6+}\) (MoO\(_3\)) were formed during the 12 hour passivation process.
- Lowered XPS binding energies of metal doped \( \text{Mo}_x\text{C} \) indicated the enriched electron density surrounding the molybdenum atom.
- Element mapping of 2% Pt-\( \text{Mo}_x\text{C} \) showed the uniform distribution of molybdenum and platinum throughout the nanowire.
- Metal doped molybdenum carbides showed higher electrocatalytic HER activity than pure molybdenum carbide.
- The high catalytic performance of Pt doped \( \text{Mo}_x\text{C} \) was due to high surface area, high uniform metal dispersion, increased number of exposed active sites, and enhanced electron transfer capability.
- Low tafel slopes around 80-90 mV/decade for Co, Ni, Cu, and Ag doped \( \text{Mo}_x\text{C} \), and 55 mV/decade for Pt doped \( \text{Mo}_x\text{C} \) displayed that \( \text{H}_\text{ads} \) desorption is the rate-determining step in the two step reaction.
- Long term stability of Pt doped \( \text{Mo}_x\text{C} \) showed negligible difference between the polarization curves of the first and 3000th cycles.
- Low loading amount of 2% Pt doped \( \text{Mo}_x\text{C} \) and high abundance of Molybdenum highlights application as a promising electrocatalyst replacement for commercial 20% Pt/C.

References