Trimetallic NiFeMoN for Electrochemical Oxygen Evolution Reaction: Facile Synthesis and Statistical Design

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Introduction

- Typical OER electrocatalysts suffer from low performance, short term stability and complicated method of synthesis.
- Ni- and Fe-based materials are promising candidates for OER and Mo-based materials improve the OER charge transfer and stability.
- It is challenging to develop a consensus on the optimum value of synthesis parameters due to a high number of experimental tests.
- **In this project, we report the one-step NiFeMoN fabrication by magnetron co-sputtering and optimize the synthesis parameters using statistical modelling.**

Material and methods

- One-step magnetron co-sputtering was employed to synthesize NiFeMoN as an Oxygen evolution reaction (OER) electrocatalyst.
- Response surface methodology model based on CCD was developed to evaluate the interaction and find the optimum percentage of Mo% and N% in the sputtered NiFeMoN.

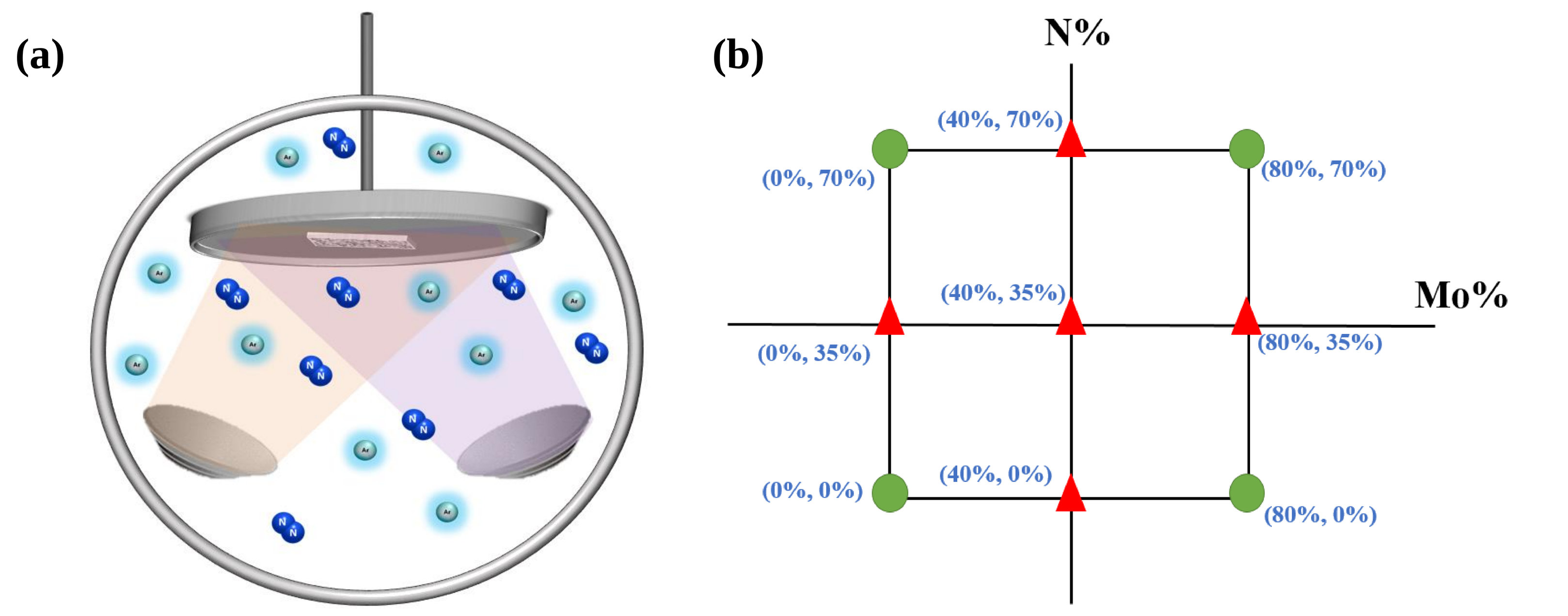

Figure 1. Schematic image of (A) magnetron co-sputtering method for NiFeMoN deposition. (B) central composite experimental design (CCD) for Mo% and N%

Result and discussion

1. Statistical model and optimization

- The coefficient of determination (R^2) and adjusted coefficient of determination (R^2_{adj}) are 96% and 93% indicating the statistical model is accurate.
- OER Overpotential hits a minimum peak by raising the N% pressure and Mo% .
- Minimum OER overpotential is gained 227 mV (216 mV with iR correction) under the optimum value of 31.35 Mo% and 47.12 N%.

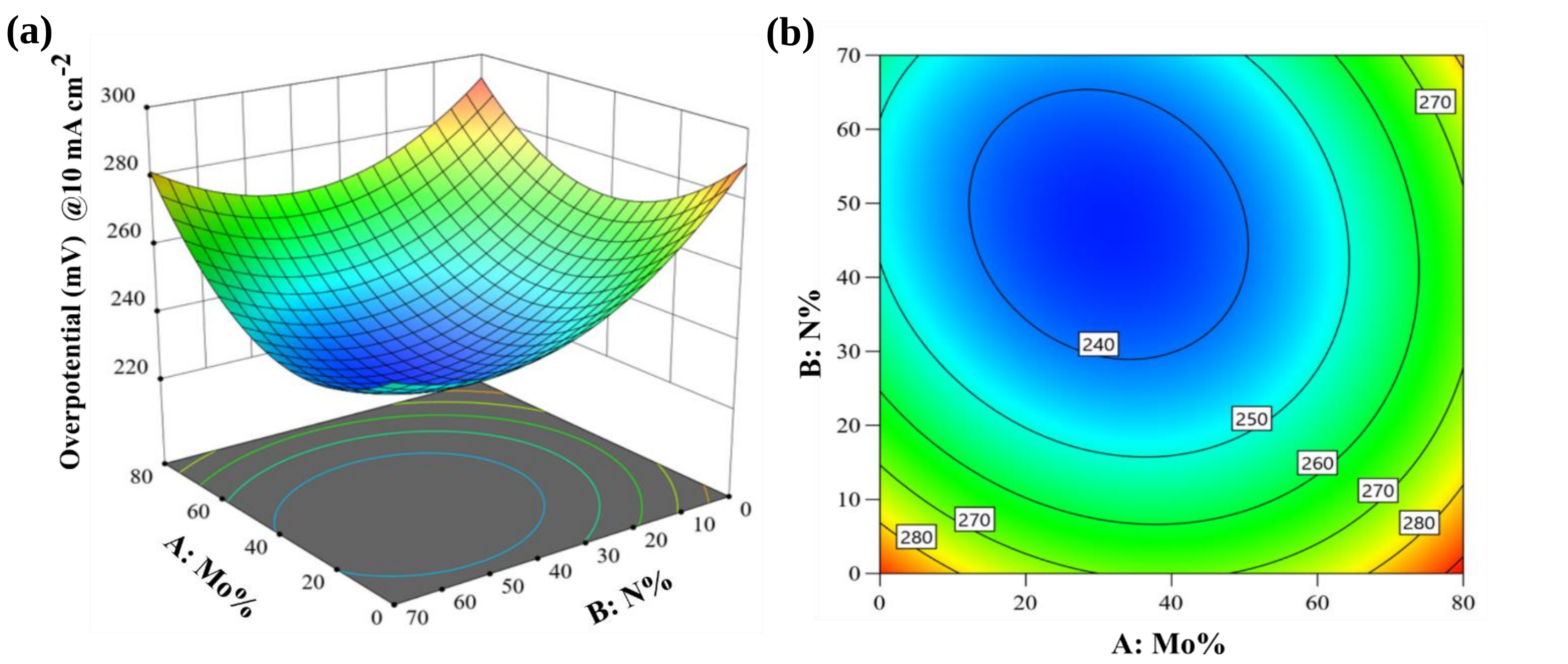

Figure 2. The response surface plots (a) and contour plot (b) of OER overpoterential at 10 mA/cm2 as a function of Mo% and N%.

2.Interaction effect of Mo% and N% on OER overpotential

- The optimum values of N% decreases from 53% to 40% upon to raising Mo% from 0% to 80%.
- The optimized point of Mo% declines from 39% to 28% by increasing N% from 0% to 70% of sputtering chamber.

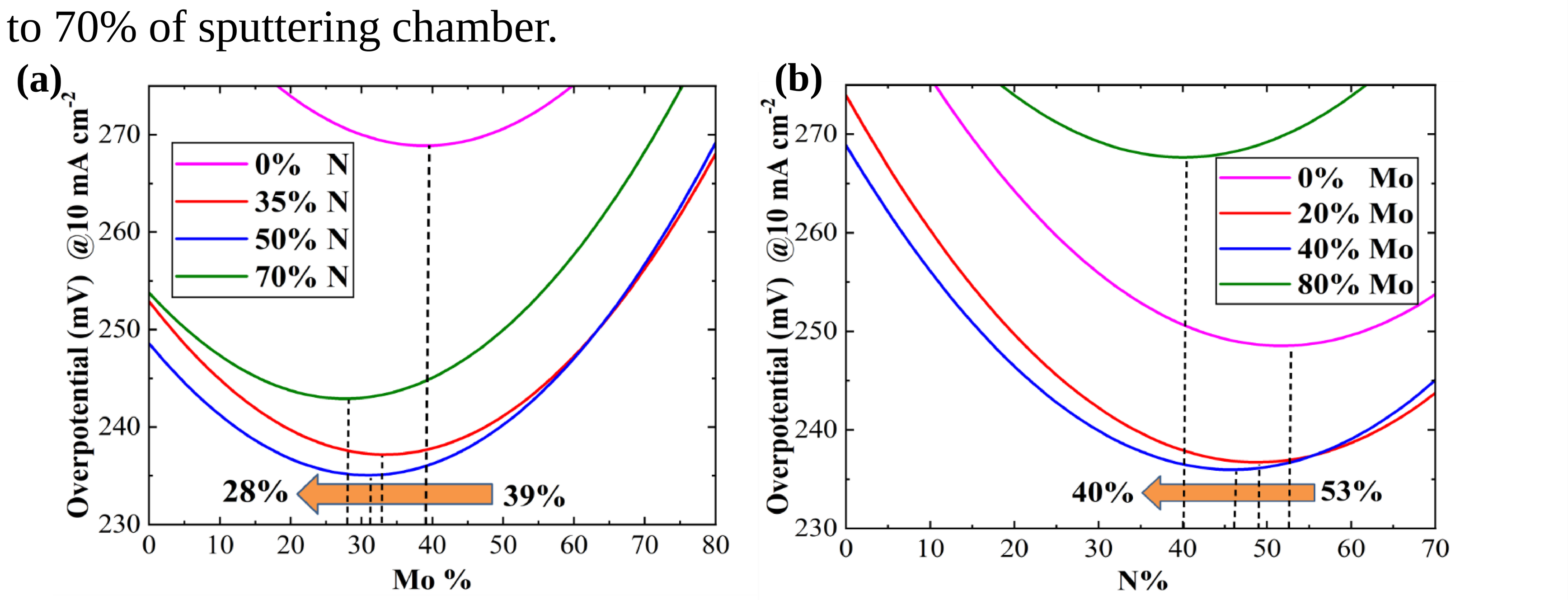

Figure 3. Variation of optimized value of Mo% at different amounts of N% (c). Variation of optimized value of N% at different amounts of Mo%.

Acknowledgments

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4. Characterization of NiFeMoN electrocatalyst

- The cross-sectional SEM shows 100 nm-thick vertical rod-shaped nanostructures of Opt NiFeMoN.
- The elemental mapping highlights the uniform distribution of Ni, Fe, Mo and N elements.

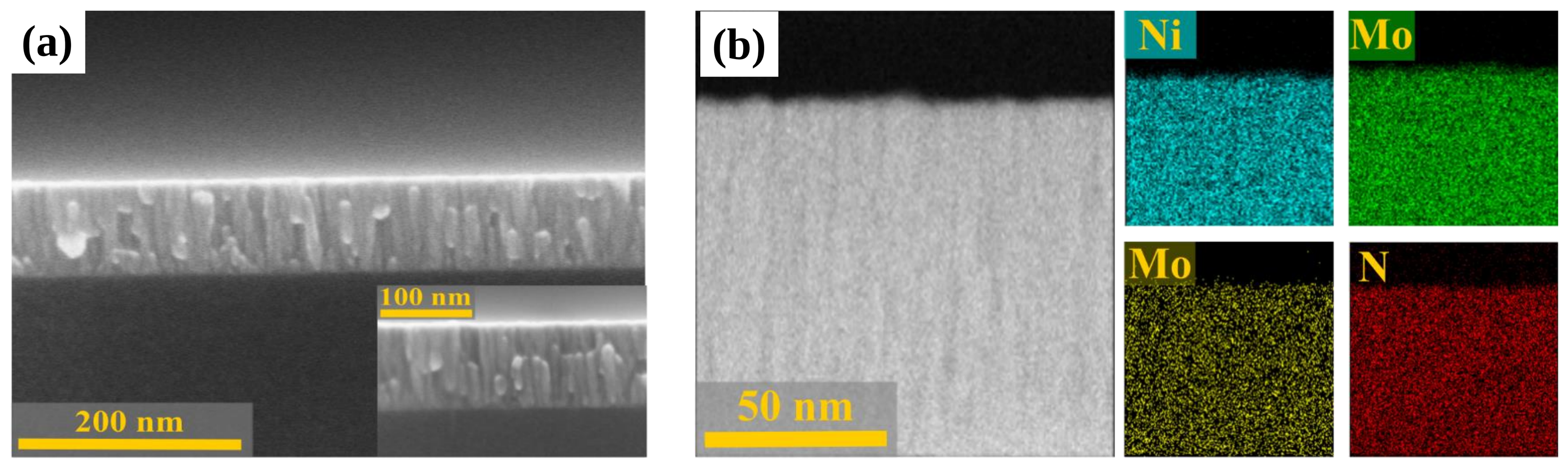

Figure 4. SEM cross-section view of Opt NiFeMoN (a), TEM image and corresponding elemental mapping of Opt NiFeMoN (b).

- Mo^{4+} and Mo^{6+} are generated by Mo addition both of which improve the OER performance.
- Mo addition caused Ni^{3+} and Fe^{3+} generation leading the OER enhancement.
- N vacancies, Ni-N and Mo-N improve the wettability, catalytic activity and stability, respectively.

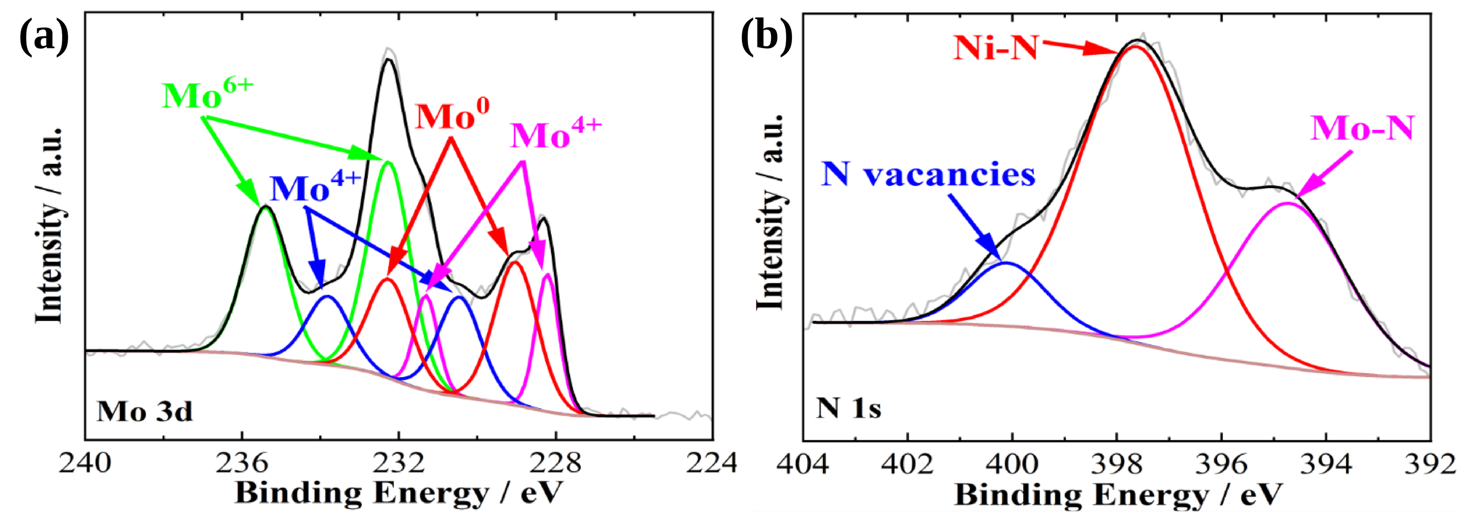

Figure 5. XPS spectra Mo3d (a) and N 1s (b) in Opt NiFeMoN.

5. Electrochemical performance of Oot NiFeMoN

- LSV curves show lower OER overpotnetial of Opt NiFeMoN compared with NiFe and Ni foam.
- Chronopotentiometry result indicates excellent stability of Opt NiFeMoN for more than 7 days.

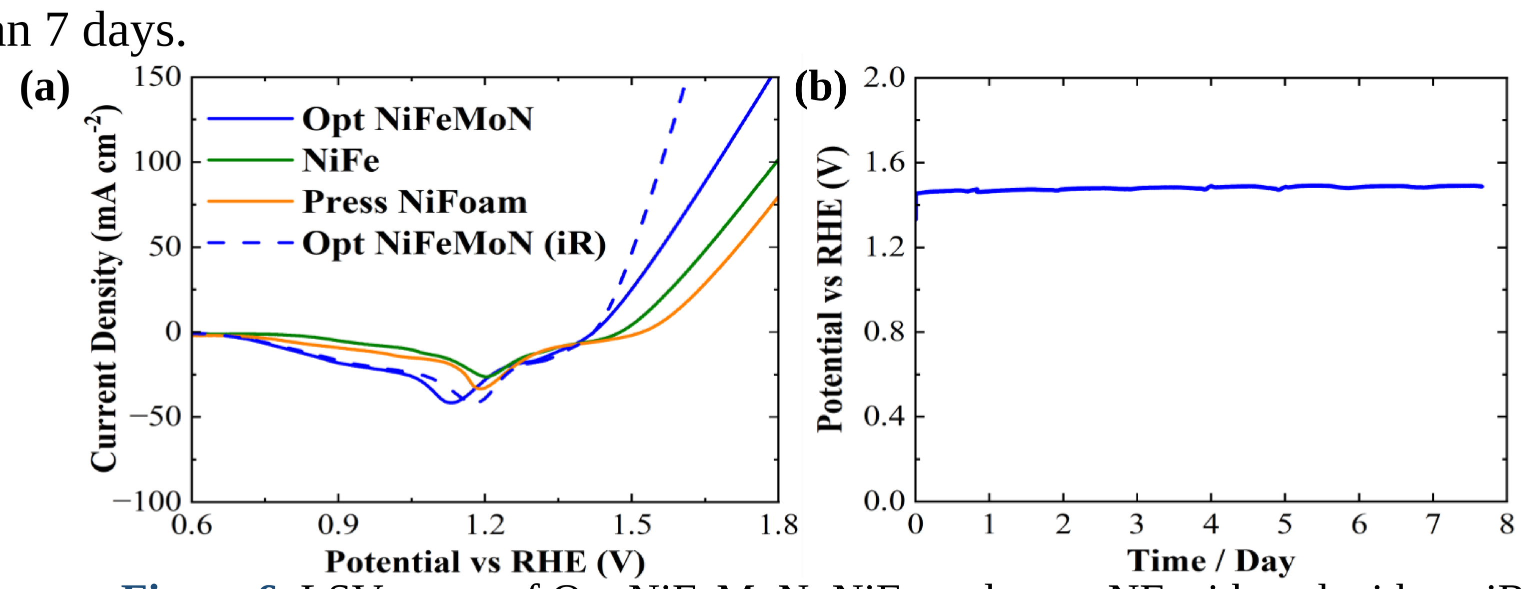

Figure 6. LSV curve of Opt NiFeMoN, NiFe and press NF with and without iR correction (a), chronopotentiometric result at 10 mA/cm^2 for Opt NiFeMoN.

6. Comparison with other OER catalysts

- Opt NiFeMoN exhibits one of the best OER performance and superior stability among other NiFeMo-based catalysts.

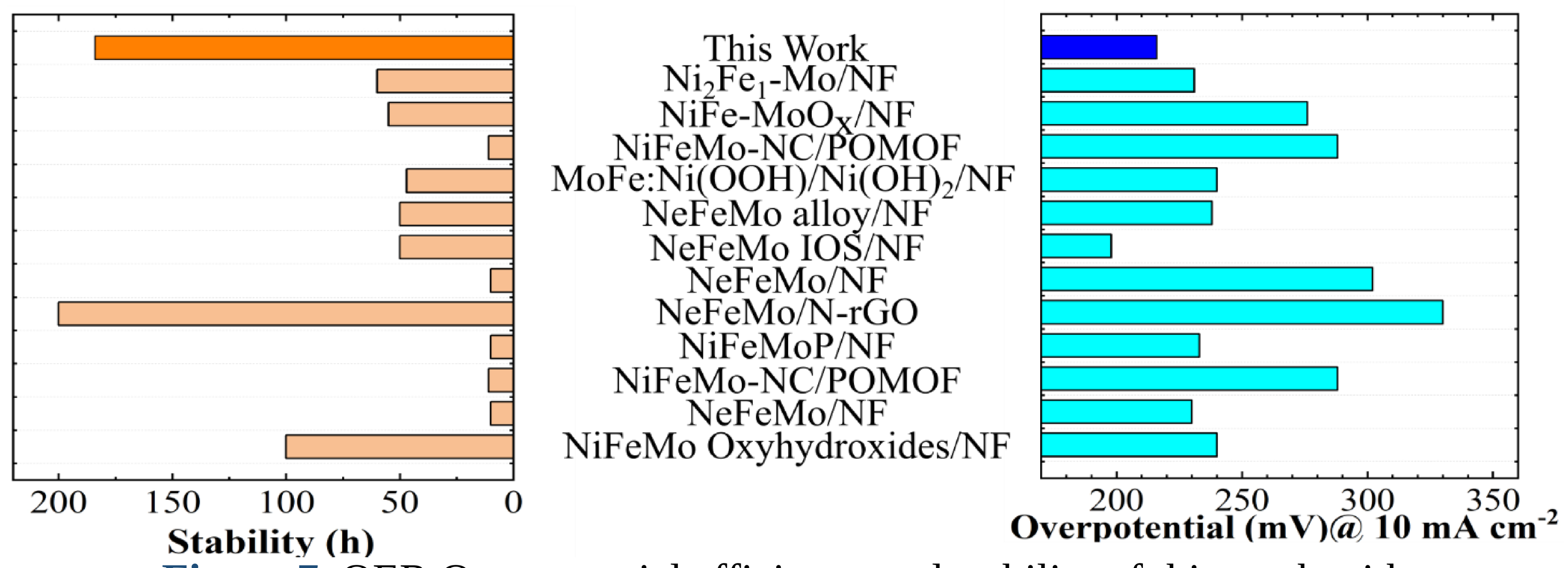

Figure 7. OER Overpotential efficiency and stability of this work with previously reported OER catalysts.

Conclusion:

- Statistical model gained by RSM and CCD shows that optimum values of Mo% and N% are interdependent.
- The Optimized values of Mo% and N% are 31.35 and 47.12.
- Opt NiFeMoN shows significant OER performance (216 mV at 10 A/cm^2) with high stability (180 h).
- Magnetron sputtering as an industry-compatible technique is expected to be to enable practical implementation of the developed catalyst for electrochemical water splitting.

References

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