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Bimetallic Nitrides on 3D Porous Nickel Foam as a Bifunctional Binder-Free Electrode for Electrochemical Water Splitting

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Goal: To reduce the overpotential of the electrode and increase the catalytic active sites by alloying transition metals

Motivation and Overview

Water is the only available carbon-free source for hydrogen production. Splitting water to produce hydrogen accounts for 4% of total hydrogen economy.

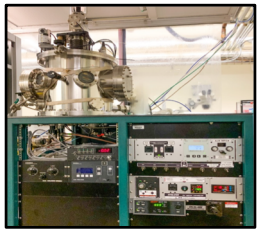
Still, the efficiency of the method is suppressed due to:

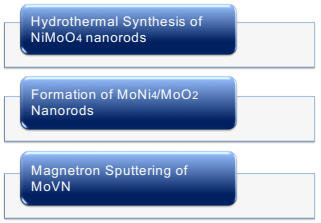
- The need for expensive and noble electrode materials.
- Electrodes for both half cell reactions requiring large overpotential.
- Reduced stability and corrosion resistance of the electrode materials.

This research works addresses the shortcomings of electrochemical water splitting and proposes a bifunctional electrode for efficient alkaline electrolysis.

Approach & Study

- Combination of Hydrothermal (Facile, control over morphology and structure) and DC/RF Magnetron sputtering (Precise control over composition and thickness) is studied.





Conclusions

- XRD results demonstrates the formation of $MoNi_4$ and MoO_2 on Ni foam after annealing
- MoVN nanoflakes have been dispersed over the nanorods
- MoVN nanoflakes on $MoNi_4$ have increased the HER and OER activity of the electrode surpassing commercial catalysts. (give some clear measure of how or how much)
- Chronoamperometry shows that the electrode has consistent performance for 12 hours without decrease in current density.

Theory

The decomposition of water (H_2O) to hydrogen (H_2) and oxygen (O_2) has a large positive free energy change (ΔE), which, in the case of electrolysis, is supplied by electrical energy. The half and overall reactions in an alkaline solution can be written as:

(Cathode) $2H_2O + 2e^- \rightarrow 2OH^- + H_2$
(Anode) $2OH^- \rightarrow H_2O + 2e^- + \frac{1}{2} O_2$
(Total) $2H_2O \rightarrow H_2 + \frac{1}{2} O_2 + H_2O$

Reaction Free energy = $\Delta_R G = \Delta_R H - T \cdot \Delta_R S$ = 286 kJ/mol

Reversible cell voltage = $U_{rev} = -\frac{\Delta_R G}{z.F}$ = -1.48 V

z = Number of exchanged electrons

F = Faraday's constant

$$E_{cell} = E_{anode} - E_{cathode} + \sum \eta + iR_{cell}$$

Hydrogen Evolution Reaction (HER)

- Consists of two electron transfer steps
- Tafel slope can be used to predict the pathway as there are only two possible mechanisms for hydrogen evolution
- The free energy of hydrogen adsorption (ΔG_H) is widely accepted to be a descriptor for a hydrogen evolution material
- By alloying metals of the left half of the transition series in the periodic table with empty or less filled d-orbitals with metals of the right half of the series with more filled d-bands, maximum bond strength and stability of the intermetallic alloy phases could be achieved.

Oxygen Evolution Reaction (OER)

- Consists of four electron/proton transfer steps
- Tafel slope cannot be used to predict the pathway as large number of intermediate steps are involved.
- Metals with variable and stable oxidation states are suitable.
- Bond strength of metal-oxide should be adequate
- Stability of oxide/hydroxides formed on the catalyst.

Results & Discussion

1.

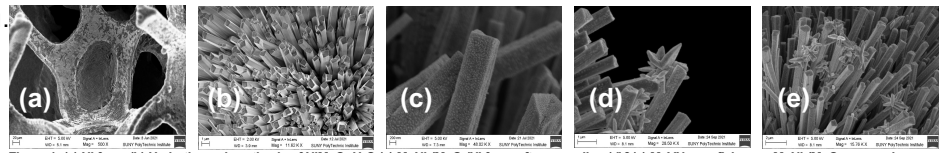


Figure 1: (a) Ni foam (b) Hydrothermal synthesis of $NiMoO_4.H_2O$ (c) $MoNi_4/MoO_2$/Ni foam after annealing (d)&(e) MoVN nanoflakes on $MoNi_4/MoO_2$ nanorods

2.

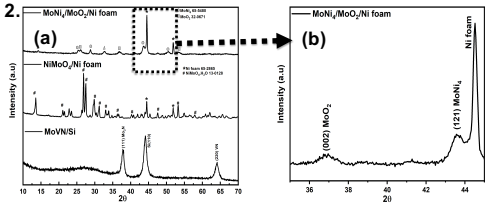


Figure 2: (a) XRD Analysis of Sputtered MoVN, $NiMoO_4$ nanorods and $MoNi_4/MoO_2$ nanorods (b) Confirmation on the formation of $MoNi_4/MoO_2$ nanorods

3.

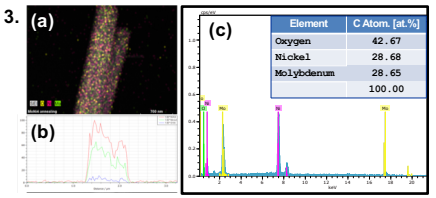


Figure 3: (a) EDS Mapping of $MoNi_4/MoO_2$/Ni foam (b) Line profile analysis (c) EDX Spectra

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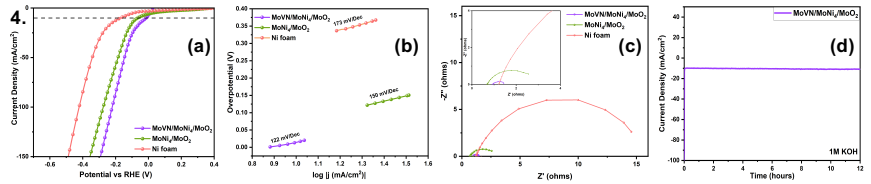

Figure 4: (HER – 1M KOH) (a) Linear sweep voltammetry curves of the electrodes (b) Tafel slope of the electrodes (c) Nyquist plot (EIS) of the electrodes (100MHz to 10 mHz) (d) Chronoamperometry curve for MoVN/$MoNi_4/MoO_2$ (at 10 mA/cm²) for 12 hours.

5.

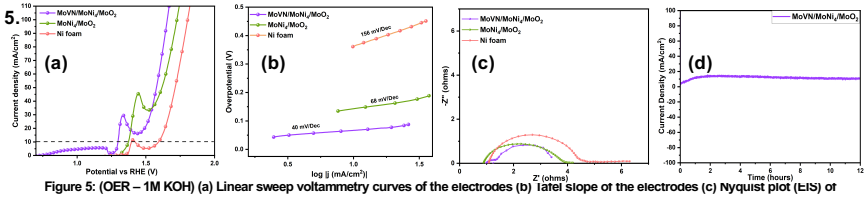

Figure 5: (OER – 1M KOH) (a) Linear sweep voltammetry curves of the electrodes (b) Tafel slope of the electrodes (c) Nyquist plot (EIS) of the electrodes (100MHz to 10 mHz) (d) Chronoamperometry curve for MoVN/$MoNi_4/MoO_2$ (at 10 mA/cm²) for 12 hours.

Future Work

- Temperature dependent Activity of the fabricated electrodes
- Testing the synthesized electrode overall voltage required for electrolysis in electrolyser setup
- Industrial Cell setup with Diaphragm

References

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