Enhanced Activity and Chlorine Protection in Prolonged Seawater Electrolysis using MoS₂/Sulfonated Reduced Graphene Oxide

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E1. Electrocatalyst Synthesis:

(a) Preparation of MoS₂ Powder

 MoS_2 Powder was prepared hydrothermally by taking molybdic acid for 'M' along with the thiourea for 'S' in the molar ratio of 1:2. This powder mixture was dissolved in 30 ml of water and 10 ml methanol and transferred into a 100 ml Teflon-lined stainless autoclave. The autoclave was heated at 180°C in an electric oven and maintained for 24 hours. The following MoS_2 powder obtained after washing with water and ethanol followed by drying.

(b) Preparation of NiS electrocatalyst:

Ni foam was carefully cleaned with concentrated HCl solution (37 wt. %) in an ultrasound bath for 5 min to remove the surface oxide layer followed by washing with deionized water and absolute ethanol. The following electrodes along with thiourea were put inside a 100 ml Teflon-lined stainless autoclave containing 30 ml of water and 10 ml methanol and heated at 180°C in an electric oven for 24 hours. The following electrode obtained after washing with water and ethanol followed by drying was named as **NiS**. This catalyst precursor was prepared to check the role of sulfur in imparting durability and activity to the electrode.

(c) Preparation of GNiS electrocatalyst:

Thiourea was in-situ deposited over RGO/NF electrode *via* the hydrothermal route following the same above-mentioned operating parameters. The electrodes were washed properly with distilled water followed by drying. The resulting electrodes were named **GNiS**. The deposition of graphene over Ni-foam followed by the in-situ formation of abundant sulphonated graphene or sulphonic groups over graphene is highly advantageous in defending component against chloride ions.

(d) Preparation of RGO/Nip electrocatalyst:

Ni plate ((foil, 20 x 20 mm) was carefully cleaned with concentrated HCl solution (37 wt. %) in an ultrasound bath for 5 min to remove the surface oxide layer followed by washing with deionized water and absolute ethanol. These electrodes were then dip coated in graphene oxide multiple times in order to develop an even layer of graphene oxide all around the Ni plate and the electrodes were dried at room temperature completely before put to use. The following electrodes obtained were placed inside a 100 ml Teflon-lined stainless autoclave containing 30 ml of water and 10 ml methanol and heated at 180°C in an electric oven for 24 hours. The electrodes obtained after washing with water and ethanol followed by drying were named as **RGO/Nip**

(e) Preparation of RGO/S/Nip electrocatalyst:

Thiourea was in-situ deposited over RGO/NiP electrode via the hydrothermal route following the same above-mentioned operating parameters. The electrodes were washed properly with distilled water followed by drying. The resulting electrodes were named **RGO/S/Nip**.



Figure S1. XRD spectra of the samples NiS powder and GNiS electrode.



Figure S2. Combined XRD spectra of the NiS and GNiS ,NiMoOS, RGO/NF and GNiMoOS electrodes.



Figure S3. The full survey XPS spectrum of GNiMoOS.

Table 1. The percentage area of peak A (162-164 eV) and B (168.8 eV) corresponding to different sulfur species in MoS₂, NiMoOS and GNiMoOS.

S.no	% area peak A (Apical S ²⁻ and Bridging S ₂ ²⁻ species of MoS2)	% area peak B (SO4 ²⁻ , SO3H-Graphene)
MoOS	72	28
Ni-MoOS	81	19
G-Ni-MoOS	7.12	92.872

E2. iR Correction Procedure

In this work, the experimental data points are manually corrected with a predetermined resistance which is obtained by fitting the high-frequency region of the electrochemical impedance spectroscopy (EIS) data with an equivalent circuit (often the Randles circuit). This resistance is then multiplied by the cell current (IR) and then substracted from the actual potential values (V_{actual} -IR). This value is then plotted with respect to the current values.



Figure S4. (a) iR drop corrected data of GNiMoOS (b)Overpotential values of the electrodes for HER before and after iR correction for 100 mA cm⁻² current density.



Figure S5. iR corrected potentials of GNiMoOS for 100 -500 mA cm⁻² current density in simulated seawater media.

E3. Determining of Electrochemical active surface area (ECSA)

Electrochemical capacitance measurements were used to determine the active surface area of catalyst. To measure the electrochemical capacitance, CV curves with various scan rates (20 mV sec⁻¹ to 100 mV sec⁻¹) were measured in non-Faradic potential window (0.5 to 0.7 V vs RHE). By plotting the capacitive currents (Δ J=Janodic -Jcathodic) against the scanning rate at the central voltage and following with a linear fit, the double layer capacitance (C_{dl}) can be estimated as half of the slope. From the double layer capacitance (Cdl) and capacitance of an atomically smooth planar surface (C_s), the ECSA was calculated using the following equation:

$$ECSA = C_{dl} / C_s$$

Where Cs is the specific capacitance for a flat surface, which was generally found to be in the range of 20-60 μ F·cm⁻².



Figure S6. (a) CV curves of GNiMoOS at different scan rates from 20 to 100 mV s⁻¹ at the potential window of 0.5 to 0.7 V vs RHE (b) ECSA linear plot of GNiMoOS.



Figure S7. Faradic efficiency % of GNiMoOS for HER and OER with time in simulated seawater.



Figure S8. SEM images of GNiMoOS at 1 μ m (a) and 100 nm (b) after 400-h durability test.



Figure S9. HER activity of GNiMoOS with varying Molar ratios of Mo:S.



Figure S10. Fitted EIS spectra of GNiMoOS.



Figure S11. Raman spectra of the NiS and GNiS electrode.







Figure S13: DFT optimized structure for adsorption Cl ion on (a) MoS₂@Gr, (b)SO₃H@Gr and (c) SO₃@Gr. Color code- C: brown, O: Red, S: Yellow, H: White, Mo: blue and Cl: Green.



Figure S14: (a)OER-LOM reaction mechanism with optimised structure for intermediates adsorbed on SO₃H@Gr. (b)Calculated free energy diagram for AEM and LOM mechanism on SO₃H@Gr. Colour code- C: brown, O: Red, S: Yellow, and H: White.



Figure S15: OER reaction mechanism with optimised structure for intermediates adsorbed on $MoS_2@Gr$. Colour code- C: brown, O: Red, S: Yellow, Mo: Blue and H:White.