Development of Graphene-Transition Metal Compounds for Electrocatalytic Reactions

Prerna Tripathi (prernat@rgipt.ac.in)
Department of Sciences and Humanities
Rajiv Ghandhi Institute of Petroleum Technology, Jais, Amethi

A wide range of electrochemical technologies, particularly in the fields of energy conversion, storage, and sensors, rely heavily on fundamental reactions like the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), the oxygen reduction reaction (ORR), and the hydrogen peroxide reduction reaction (H_2O_2RR). These days, transition metal compounds (TMCs), such as transition metal oxides, phosphides, sulphides, nitrides, carbides, and selenides, are thought to be promising materials for electrocatalytic reactions because of their remarkable catalytic capabilities and plentiful reserves. Nevertheless, despite TMC's outstanding performance, various approaches like catalysts based on precious noble metals are still proven to be more effective. To enhance TMC's electrocalytic performance, hybrids with graphene-based materials, TMC phase and structural alteration, and heteroatom-based chemical doping have all been studied. Graphene-TMC hybrids, materials made by fusing graphene with transition metal compounds, hold enormous potential in improving properties of TMC. It helps with H^+ adsorption, increases electrochemical conductivity, decreases charge-transfer resistance at the catalyst/electrolyte contact, and shields the catalyst from poisoning. The present work has been divided into six chapter.

Chapter 1: In this chapter, we give a brief introduction of Transition metal compounds (TMCs) and TMCs-graphene derived electrocatalysts. An overview of the fundamental principles as well as the parameters used to assess the performance of electrocatalytic reactions has been discussed. Finally, the chapter summarises the works in the development of transition metals-graphene compounds.

Chapter 2: Hydrogen production *via* acidic water splitting is of great importance in electrolyzer industries. In this chapter, synthesis of self-assembled, freestanding, three-dimensional (3D) graphene- non-noble tungsten oxide (SA-GWO) electrode with remarkable electrocatalytic activity in acidic media has been summarized. Bi-functional (HER and OER) acidic H_2O electro-splitting has been attainable by SA-GWO electrodes at full potential of ~1.90 V, 10 mA/cm^2. Remarkably, it also exhibited oxygen evolution (OER) activity in the acidic medium. Most importantly, the WO_3 polymorph, typically responsible for the distinct mechanism of HER and OER action in 1M H_2SO_4, has been identified and proven. Graphene served as a stable foundation for creating independent 3D SA-GWO electrodes

through a straightforward self-assembly method, eliminating the need for extra binders. This approach reduced cost and ensured the electrocatalyst's durability and mechanical robustness.

Chapter 3: This chapter reports the development of a double-layer anode that is composed of a molybdenum sulphide electrocatalyst layer that is uniformly deposited over a Sulfonated Graphene-Ni foam electrode (G-Ni-MoOS) using a straightforward one-step hydrothermal method. The in-situ-generated polyatomic sulfate ions imbibed over the graphene sheets having repellant properties towards chlorine along with contribution from GO towards conserving the mechanical integrity during OER, were responsible for activity, durability, and superior corrosion resistance of the seawater-splitting anode. The successful in-situ functionalization of sulphonic moieties onto the graphene oxide skeleton of the GNiMoOS electrode has been confirmed by XPS, RAMAN, SEM, TEM, and IR techniques. The density of states (DOS) and DFT calculations clearly validated the preference of sulphonic moeities towards OH^- compared to Cl^- ions. Outstanding and stable OER and HER activities in harsh sea have been observed at a very low overpotential of 180 and 165 mV, respectively, to reach current densities of 100 mA cm^{-2} at 27^oC ^oC.

Chapter 4: This chapter describes the synthesis of three-dimensional (3D), self-assembled and freestanding graphene-based sulphide (MoOS-G), selenide (MoOSe-G), and oxide (MoO-G) electrodes for the application of HER. All the self-assembled electrode systems found active in H_2SO_4 media for HER, it is observed that among all the systems, the most active sulphide electrode (MoOS-G) has displayed a current density of 25 mA/cm^2 at 350 mV at room temperature. None of the electrodes found stable under alkaline KOH medium due to dissolution with time during anodic polarizations. The resulting low-cost freestanding MoOS-G worked amazingly well, with a current density of 35 mA/cm² at 25 °C in cells with two electrodes. Sulphur with a purity of ~99% has been produced by the selective electrolysis of H_2S. The developed 3D electrodes have been well characterised by TEM, SEM-EDAX, RAMAN, and XRD techniques.

Chapter 5: In this chapter, the synthesis of palladium incorporated nitrogen doped graphene oxide nanospheres (Pd-N-GO) for the application of ORR and H_2O_2RR has been presented. SEM, TEM, IR, XRD, RAMAN and XPS confirm the successful incorporation of palladium into the base structure of graphene nanospheres. The electrochemical reduction of oxygen on Pd-N-GO catalyst in alkaline solutions, along with its detailed mechanism has been investigated using the rotating ring-disk electrode (RRDE) method. The RRDE results indicated that Pd-N-GO catalyzes a 4-electron reduction of oxygen whereas the bare N-GONs reduces oxygen *via* a two-electron pathway in

alkaline medium. Furthermore, a screen-printed electrochemical sensor (Pd-N-GO/SPCE) was fabricated via the drop-casting of Pd-N-GO over SPCE for the sensitive electrochemical detection of H_2O_2 *via* H2O2 RR, it exhibited an excellent detection limit (LOD) of 260 µM with a decent sensitivity of 0.055 $\mu A \mu M^{-1} cm^{-2}$. In addition, Pd-N-GO/SPCE also showed excellent selectivity, repeatability, and stability for detecting H_2O_2.

Chapter 6: In this chapter, based on the current studies, we have drawn conclusions, discussed future directions for the work, and provided key recommendations.

Publications from the Present work:

- **P. Tripathi**, A. K. Verma, A. Vishwakarma, K. Mitra, B. Ray, A. S. K. Sinha, S. Singh, "*Fabrication and Evaluation of a Self-standing Reduced Graphene-tungsten Oxides Hybrid Electrode for Acidic Water Splitting",* **International Journal of Hydrogen Energy**,47, 86, 2022, 36381 – 36396.
- **P. Tripathi**, A. K. Verma, A. S. K. Sinha, S. Singh, *Graphene-Transition Metal Electrocatalysts for Sustainable Water Electrolysis,* Wiley **ChemistrySelect** (2024). (DOI:10.1002/slct.202403155)
- **P. Tripathi**, A. K. Verma, A. S. K. Sinha, S. Singh, *Cutting -Edge OER Electrocatalysts for Sustainable Seawater Electrolysis,* **ACS Energy & Fuels** (2024) *(accepted)*
- **P. Tripathi**, A.K. Verma, R. Shakir, J. Karthikeyan, A. S. K. Sinha, S. Singh, *"Sulphur and Graphene Synergistically acting as durability booster for sea water electrolysis"* (2024) *(Manuscript submitted)*
- **P. Tripathi**, A.K. Verma, A. S. K. Sinha, S. Singh, *"3-D Self Assembled Graphene Molybdenum Sulfide as Cathode Material for Selective Electrochemical Cathodic Decomposition of Hydrogen Sulfide"* (2024) *(Manuscript under preparation)*
- **P. Tripathi**, A.K. Verma, A. S. K. Sinha, S. Singh, *"Fabrication of Nitrogen-Doped Graphene Oxide Nanosphere with Palladium Embedded for Multipurpose Application*". (2024) *(Manuscript under preparation)*
- A. K. Verma, **P. Tripathi**, A. S. K. Sinha*, S. Singh*, *Advanced Materials in Energy Conversion Devices: Fuel Cells and Biofuel Cells***, Scrivener Publishing, Wiley** (ISBN: 9781394185818), **2023**, 273 – 284. (Book Chapter)
- Patent: "*Layered electrode for seawater electrolysis*" (**Indian Patent Application No. 202211011767**). NETRA 2022.
- Patent: "*Molybdic transformation to efficient catalyst systems for sea water electro splitting and generation of hydrogen and oxygen*" (**Indian Patent Application No. 202311053855**). NETRA 2023.