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# Developing Novel Electro-catalysts for Green Hydrogen Generation

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## Where we are in Electro-catalysts for Green Hydrogen production:

Hydrogen energy today is proving to be an ideal alternative to fossil fuels because of its versatile applications. However, generating and utilizing hydrogen as a fuel requires huge investments pertaining to critical infrastructures. Green hydrogen stands for generating hydrogen by water splitting technique utilizing renewable sources of energy. Hydrogen produced by this technique is in the purest form and can be subsequently converted into electricity using a fuel cell. Oxygen is a byproduct of water electrolysis, which can be utilized in medical and chemical industries. Today, only 4% of total global hydrogen production is via electrolysis using renewable energy sources. This is due to the economic factors associated with utilizing renewable energy sources. This trend is expected to change, as most of the European countries as per the European Energy Directive are covering 14% of their energy requirements by renewable energy sources.

**Public Interest Statement**

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

The role of an electrocatalyst is to break barriers in kinetic energy during electrochemical reactions. The ideal properties of an electrocatalyst are low overpotential, high active surface area, high electrical conductivity, chemical and mechanical stability. Scientific hydrogen generation from water electrolysis features two types; proton exchange membranes (PEM) and alkaline electrolysis. PEM stands for performing water splitting under acidic conditions and alkaline electrolysis under alkaline conditions. PEM technology displays about 2 to 3 times higher efficiency than alkaline electrolysis.

Volcano plots, used for the comparison of different metal electrocatalysts, indicate Platinum (Pt) to be having the highest exchange current density in both acidic and alkaline media. Pt is followed by Rhodium (Rh), Iridium (IR) in the volcano plots. Hence, Pt, Ir and Rh are considered as the classic catalysts for electrolysis of water. But these noble metals are very expensive to be used as an electrocatalyst. Therefore, researchers around the world are looking to develop sophisticated electrodes that act as an electrocatalyst. The role of these electrodes will be to increase the operational surface area, thereby increasing the efficiency of the process.

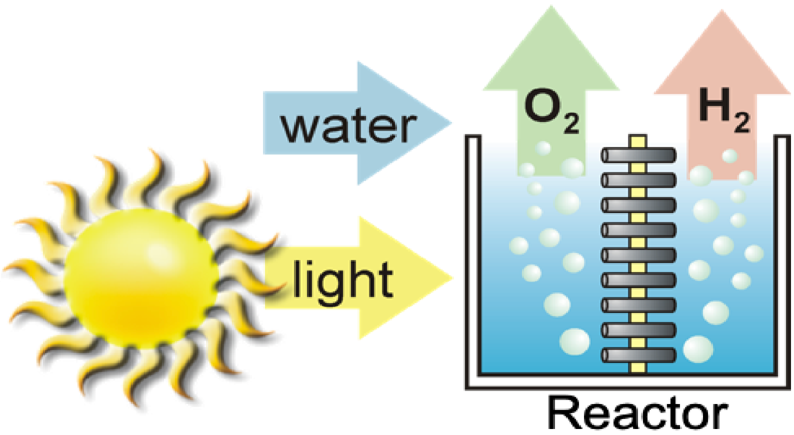


**Fig 1.** Fuel from Water splitting (illustration)

The process of water electrolysis comprises two half-cell reactions; oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The major challenge for electrocatalysts of both OER and HER in alkaline and PEM electrolyzers is the reduction of overpotential. HER in PEM follows a three step process as shown in equation 1 to 3;

i) Volmer Step to produce adsorbed hydrogen.

$$H^{+} + e^{-} = H_{ad} \quad (1)$$

ii) Heyrovsky step to produce hydrogen

$$H^{+} + e^{-} + H_{ad} = H_{2} \quad (2)$$

iii) Tafel step to produce hydrogen

$2H_{ad} = H_2$ (3)

HER in alkaline media is however a two step process as shown in equations 4 and 5.

i) Volmer Step to produce adsorbed hydrogen.

$H_2O + e^- = OH^- + H_{ad}$ (4)

ii) Heyrovsky step to produce hydrogen

$H_2O + e^- + H_{ad} = OH^- + H_2$ (5)

OER follows adsorbate evolution mechanism (AEM) as represented in equations 6 to 9;

$OH^- + M = M - OH + e^-$ (6)

$M - OH + OH^- = M - O + H_2O + e^-$ (7)

$M - O + OH^- = M - OOH + e^- / 2M - O = 2M + O_2 + 2e^-$ (8)

$M - OOH + OH^- \rightarrow O_2 + H_2O + e^- + M$ (9)

Catalysts for HER are usually categorized broadly as noble metal and non-noble metal based electrocatalysts. Most common noble metal based electrocatalyst for HER is Pt. Efforts are being made to alloy Pt with low-cost transition metals and water dissolving promoters to improve the HER performance and reduce the cost. Research focus is nowadays shifting towards developing earth abundant and low cost non noble-metal based electrocatalysts. Some of the novel catalysts for HER being developed and investigated from literatures include PtNi–Ni NA/CC, PtNi–O/C, PtNi(N) NW, $Mo_2C$-R, $Mo_2C$-GNR, Ni2P/Ti, $NiCo_2P_x$, Defect-rich $MoS_2$, $CoS_2$ NW, $CoS_2$ MW and Oxygenated $MoS_2$.

Similar to HER, OER electrocatalysts are also categorized broadly into noble and non-noble metal based catalysts. Noble metals used for OER include Ru, Ir, Rh, Au, Pt, and Pd-based catalysts. In order to improve the efficiency and reduce the cost of these catalysts, mixed oxides are being investigated. They are usually known as bi/tri- functional catalysts. Among the non-noble metal based category earth abundant oxide and (oxy) hydroxide electrocatalysts are being studied to a great extent. Few novel electrocatalysts for OER investigated from literatures include Cu-doped $RuO_2$, IrNi NPNW, IrCo NPNW, IrFe NPNW, IrNiCu DNF, IrO2 NN, $Au_{40}Co_{60}$ NPs, G-FeCoW, Plasma-engraved $Co_3O_4$, NiFe-LDH NPs, $Ni_{0.83}Fe_{0.17}(OH)_2$ and $Ni_xFe_{1-x}Se_2$-DO.

The choice of electrocatalysts also depend on the nature of electrolyzer i.e PEM or alkaline. Table 1 represents the broad categorization of novel electrocatalysts for HER and OER being developed and studied based on the electrolyzers.

Table 1 : Broad novel-electrocatalyst groups

| Novel Electrocatalysts | | | |
|---|---|---|---|
| **OER** | | **HER** | |
| **PEM** | **Alkaline** | **PEM** | **Alkaline** |
| 1. Mixed oxides<br>2. Oxidation-resistant supports. | 1. Ni oxides<br>2. Co oxides<br>3. Fe oxides<br>4. Mn oxides<br>5. Perovskite (in the form of $ABO_3$*) | 1. Pt- Based<br>2. Sulfides<br>3. Phosphides<br>4. Carbides<br>5. Nitrides | 1. Ni- Based<br>2. Co- Based<br>3. Fe- Based |

* (A- Larger cation comprising of lanthanide, alkaline or alkaline-earth elements and B-Smaller cation with 3d, 4d and 5d configurations)

Mixed metal oxides are high performance electrocatalysts developed by easy dip coatings on foams. Oxidation-resistant supports produced by doping helps in better interactions between support and Pt catalyst increasing Pt oxygen reduction reaction activity. Single crystalline nanoporous NiO is produced by hydrothermal, soft-templated synthesis route followed by calcination to develop a highly active electrocatalyst for OER. Co oxide coatings are developed by electrodeposition from a $Co^{2+}$ containing electrolyte. Fe oxides are produced by a hard templating method. The unique features of this catalyst is low overpotential and high current density. Mn oxides are developed by thermal decomposition and annealing techniques. They exhibit lower overpotential compared to $RuO_2$ and $IrO_2$ electrocatalysts. Nanostructures perovskites have tremendous potential for electrocatalytic reaction, however, producing them is a major challenge.

The most effective HER electrocatalyst as of today is Pt. However, its high cost and scarcity hinders its broad utilization. Transition metal sulfides (TMS) are an ideal alternative to precious metals in water splitting reaction. TMS are prepared by sol–gel method followed by sulfurization forming a mesoporous structure. Transition metal phosphides (TMP) display excellent electrocatalytic activity on HER due to their short/medium range ordered structure with abundant active sites. TMP are developed by hetero-atom doping or alloying forming porous hetero-structures. Metal Carbide electrocatalyst are developed by two - step oxidation – carburization reaction used as electrodes. Metal carbide electrocatalysts possess excellent HER properties by the Volmer-Heyrovsky mechanism. Transition metal nitrides (TMNs) -based composites in combination with other metals and carbon materials have been demonstrated to possess improved catalytic properties due to modified electronic structure leading to balanced M–H bonding strength, synergistic effects, and electrochemical stability.

Ni based alloy and hetero-structures exhibit excellent catalytic properties due to their surface adsorption properties. They are usually developed by cathodic electrodeposition method. Co based electrocatalysts are widely investigated as a bifunctional electrocatalysts because of their electrochemical capabilities and structural adjustability during doping. Fe is usually used as a bifunctional electrocatalyst for HER reaction by doping with various metal oxides like $MoO_2$/$MoO_3$ sheets. They display outstanding stability for a longer duration practically.

The catalytic activity of HER and OER electrocatalysts can be further improved by modifying the structure of electrocatalyst. Some of the latest observations in this direction includes developing single atom crystals (SACs), nanowires, nanoframes and core-shell structure of nanoparticles for HER and OER reactions. Developing nanostructured electrocatalysts tend to increase the atom utilization energy (AUE) and high specific area.

The structure, texture and morphology of the electrocatalysts developed are very complex in nature and require advanced characterization techniques to determine its effectiveness. Some of the characterization techniques used to study the nature of electrocatalysts include X-ray diffraction (XRD), transmission electron microscopy (TEM), laser Raman spectroscopy (LRS), N2-physisorption, hydrogen temperature programmed reduction (H2-TPR), thermogravimetric analysis (TGA), atomic absorption spectrometry (AAS), Scanning Electron MIcroscope (SEM), temperature-programmed oxidation experiments(TPO), Bru-nauer, Emmett and Teller (BET), Inductively coupled plasma spectroscopy (ICP), Thermogravimetric and differential thermal analysis (DTA/TG), X-ray photoelectron spectroscopy (XPS), Field Emission Scanning Electron Microscope (FESEM) and Barret–Joyner–Halenda (BJH) method.

## Concluding Remarks

The main goal of developing novel electrocatalysts are to reduce overpotential, reduce tafel slope, increase exchange current density and efficiency which are stable for a long period of time. The stability is characterized by the change in current or overpotential over time and the efficiency is characterized by comparison between experimental and theoretical values (i.e turnover frequency and faradaic efficiency. This is a crucial step towards practical application of water splitting techniques in industries. Understanding the present reaction mechanisms and identifying the limitations could lead to new advances towards better design of electrocatalysts.

Based on the above observations on novel electrocatalysts for HER and OER processes, there is tremendous scope for research in following areas for designing an electrocatalyst for industrial applications;

- Developing low cost catalyst synthesis methods.
- Optimizing catalytic activity.
- Computational analysis of relationship between catalytic structure and activity.
- Modifying the crystal structure of electrocatalysts.
- Large scale preparation of electrocatalysts and examining it for long term operations.

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