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Chapter

Recent Trends in Development of Metal Nitride Nanocatalysts for Water Electrolysis Application

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Abstract

Nanocatalysts for sustainable water electrolysis is strongly desirable to promote the commercialization of H_2 as the alternate clean energy source for the future. The goal is cheaper hydrogen production from sea and low grade water by minimizing the energy consumption and using low cost cell components & non-noble metal catalysts. The conductivity of metal nitrides and their ability to carry out Hydrogen Evolution Reaction and Oxygen Evolution Reaction at relatively low overpotential render these one of the frontline candidates to be potentially utilized as the catalyst for low cost H_2 production via electrolysis. In this chapter, the potential of metal nitride catalyst towards fulfilling the above objective is discussed. The synthesis of various metal nitride catalysts, their efficiency towards electrode half reactions and the effectiveness of these class of nanocatalyst for electrolysis of sea water is elaborated. A review of recent literature with special reference to the catalyst systems based on non-noble metals will be provided to assess the likelihood of these nanocatalyst to serve as a commercial grade electrode material for sea water electrolysis.

Keywords: metal nitride, nanocatalyst, water electrolysis, hydrogel evolution reaction, oxygen evolution reaction

1. Introduction

Low cost, robust alkaline electrolyzers employ non-noble metals as electrodes and allow sustainable electrolysis of water for generation of H_2 at a commercial level. The goal is cheaper hydrogen production by minimizing the energy consumption and using low cost cell components. The important factor for consideration here is the use of sea water for H_2 generation in the cell environment. Sea-water and ground water are multicomponent natural electrolytes with alkali chloride as the main component. However, the major issue with such water electrolysis is the production of toxic chlorine gas (Cl_2) at the anode along with O_2 gas. Oxygen evolution reaction (OER) involves a four electron transfer, which makes it much more difficult to catalyze compared to the chlorine evolution reaction (CER), where only a two electron transfer is involved. There have been several attempts to suppress CER during saline water electrolysis such as use of special catalysts that favor OER over CER, coating the anode with protective layers to prevent it from adsorption of chloride ion, and salting out NaCl from the electrolyte solution. Another problem of using sea water or high TDS water is the precipitation of hydroxides of magnesium and calcium on electrode surfaces due to alkaline nature of cathode. Removal of calcium and magnesium prior

to electrolysis involve additional cost and generation of solid wastes. Therefore, prevention of precipitation of hydroxides is necessary to run the electrolyzer smoothly for a long period. Recent studies show that formation of Mg^{2+} and Ca^{2+} precipitate on the electrode can be overcome by operating the electrolyzer at near neutral pH, which would also enable the use of low cost earth-abundant electrocatalysts.

2. Metal oxide and hydroxide based catalysts for electrolysis

Metal oxides were the first generation of catalysts synthesized and studied to facilitate sustained electrolysis of water for H_2 generation. Bennet reported anodes based on MnO_x that exhibit high selectively towards OER over CER in acidic saline water [1]. Since then, many oxides and (oxy)hydroxides (-OOH) of first-row transition metals have been investigated for OER as low-cost alternatives to the noble metals. Kato and coworkers evaluated Mn-based mixed metal oxides quoted on an IrO_x/Ti surface and the catalyst system exhibited nearly 100% selectivity towards OER [2]. Strasser and co-workers used NiFe layered double hydroxide nanoplates as OER selective electrocatalysts in seawater. However, the selectivity was limited within over potential range of <480 mV at current density value of 10 $mAcm^{-2}$ [3]. Koper and co-workers used the strategy of depositing a thin MnO_x film onto IrO_x on glassy carbon support that moderately decreased the catalytic activity and strongly shifted the product selectivity from Cl_2 towards O_2. The MnO_x deposit was catalytically inactive and instead seemed to function as a diffusion barrier that prevented Cl^- ion from reacting on the IrO_x catalyst surface present below, while ensured the transport of water, H^+, and O_2 between IrO_x and the electrolyte solution required to maintain OER activity [4]. Overall, the issue with oxide and hydroxides was the overpotential value that render the CER as competitive reaction along with OER. As can be seen in the **Table 1** below, the overpotential value with most of the hydroxides were on the higher side.

Catalysts	Electrolytes	Overpotential (mV) at Specific Current Density	Tafel Slope (mV dec^{-1})
NiOOH	0.1 M KOH	375@ 5 $mAcm^{-2}$	—
γ-$Ni_{0.87}Fe_{0.13}OOH$	0.1 M KOH	390@ 10 $mAcm^{-2}$	—
γ-$Ni_{0.75}Fe_{0.25}OOH$	0.1 M KOH	370@ 10 $mAcm^{-2}$	—
NiFe-LDH	1.0 M KOH	300@ 10 $mAcm^{-2}$	40
NiCo-LDH	1.0 M KOH	335@ 10 $mAcm^{-2}$	41
FeNi-rGO LDH	1.0 M KOH	195@ 10 $mAcm^{-2}$	39
FeNi-GO LDH	1.0 M KOH	210@ 10 $mAcm^{-2}$	40
NiCr-DH	0.1 M KOH	310@ 1 $mAcm^{-2}$	—
NiMn-DH	0.1 M KOH	380@ 1 $mAcm^{-2}$	—
NiFe-DH	0.1 M KOH	270@ 1 $mAcm^{-2}$	—
NiCo-DH	0.1 M KOH	500@ 1 $mAcm^{-2}$	—
$Ni(OH)_2$	0.1 M KOH	410@ 1 $mAcm^{-2}$	—
NiCu-DH	0.1 M KOH	450@ 1 $mAcm^{-2}$	—
NiZn-DH	0.1 M KOH	>500@ 1 $mAcm^{-2}$	—

Table 1.
The OER overpotential value of metal hydroxide catalysts reported in recent literature. (reproduced with permission from Ref. [5] Copyright 2019 WILEY-VCH Verlag GmbH).

From the above discussions, it is apparent that major technical challenges that hinder the progress of sea-water/ground-water splitting are the Cl_2 gas evolution and the deposition of insoluble $Mg(OH)_2$ and $Ca(OH)_2$ precipitates. Suppression of CER at high current density is possible by using an active electrocatalyst which works for OER below the overpotential of CER. Additionally, use of ultrathin coatings based on SiO_2 or TiO_2 can selectively block Cl^- ions and thereby suppress the undesirable CER. Precipitation process can be overcome by maintaining the pH at or near neutral value as pKa for the $Mg(OH)_2$ and $Ca(OH)_2$ precipitation reactions are 10.8 and 12.5, respectively. Therefore, it is imperative to develop more advanced electrolyzer systems that can split such waters efficiently and cost-effectively at or near neutral pH environment. Various strategies were adopted to address the issue of CER through development of suitable catalyst system. For example, Dai and coworkers have recently developed a $NiFe/NiS_x/Ni$ anode for active, stable and long term seawater electrolysis [6]. The Ni foam was uniformly electrodeposited with NiFe possessing an underneath NiS_x interlayer served as a highly selective OER catalyst for seawater splitting under alkaline condition, the conductive interlayer based on Nickel sulfide provided the stability to the electrode against Cl^- corrosion and degradation. This seawater electrolyzer working under a potential of 2.1 V achieved current density value of 400 mA/cm^2 in seawater electrolyte under room temperature conditions. The stability test revealed that no loss in activity was noticeable up to 1000 h. In spite of the significant efforts to develop electrocatalysts for HER and OER, to the best of our knowledge, there is no commercially available electrolyzer that can split sea water or high total dissolved solid (TDS) containing water into H_2 and O_2. Abundance of Ni is ample superior (90 ppm in nature) compared to other transition metals and the cost is ~4000 times lower compared to that of the benchmark Pt. Therefore, the aim is to design low cost affordable sea water electrolyzer using non-noble metal based nitride/phosphide/sulfide/carbide/graphene nanocatalysts. The chapter especially focuses on the development of nitride based affordable catalyst systems to understand the state of the art and the promise associated with such catalyst system towards catalyzing sustainable sea water or low value water in a sustainable manner.

3. Synthetic procedure for metal nitride based catalyst

The most widely used method for the preparation of nanostructured metal nitrides is via heating the corresponding oxides and hydroxides in the presence of different nitrogen sources such as NH_3, N_2, NH_2NH_2, urea, and dicyanamide [7–9]. For the synthesis of binary metal nitrides such as Mo_2N, and Fe_xN etc., NH_3 is frequently used as the nitrogen source with heat treatment between 400 and 1000°C. The heating rate, gas flow rate and reaction time typically controls the composition of resulting catalyst. For example, heating molybdenum oxide with NH_3 at a flow rate of 100 mL/min at 700°C for 2 h produced Mo_2N [10]. In this procedure, the metal salt along with a polymer (PVP) was dispersed in DMF to form an uniform coating on the substrate before heat treatment. As per the SEM and TEM data, the coating of nitride catalyst on the Ni foam was uniform. The procedure was effective to produce crystalline Fe and Ni nitrides. Importantly, optimization in reaction condition is necessary to control the nanostructure of the catalyst, that is important for improved catalytic activity. For example, liquid exfoliation and templating are used to prepare ultrathin 2D nanosheets [11]. Liquid exfoliation is a relatively simpler technique, in which the bulk metal nitride synthesized is added to a high polar solvent such NMP, and the mixture is ultrasonicated to exfoliate the catalyst to nanosheets. For example, a solvent exfoliated atomically thin MoN nanosheet demonstrated improved HER activity compared to that of the as prepared catalyst [12].

Similarly, N_2 is another nitrogen source used for synthesis of metal nitride via calcination process and plasma treatment [13]. The ternary metal nitrides are prepared from the ternary metal oxides via treatment with a nitrogen source [14]. In many of the reports, the metal oxides are utilized as the precursor for the corresponding nitrides and the resulting nitride catalysts have mimicked the structure of the oxide precursor. For example, the electrocatalytic Ni-Mo nitride nanotubes were synthesized by heating $NiMoO_4$ nanotubes under NH_3 atmosphere at 550°C. The first step involved the synthesis of Ni-Mo bimetallic oxide nanorods under heat treatment in presence of air. Subsequently, the $NiMoO_4$ was converted to NiMoN in presence of NH_3. Metal hydroxides are another option for being used as the precursor in metal nitride synthesis. The advantage with the hydroxides is that the metal hydroxides require lower temperature compared to that of the oxide precursors for conversion. For example, Ni_3FeN was successfully synthesized by nitridation reaction with the corresponding double hydroxide precursors in presence of NH_3. The Ni_3Fe layered double hydroxides were heated at 400°C to prepare the Ni_3FeN nanoparticles. The SEM images supported a change in surface morphology after ammonia treatment and the TEM displayed lattice spacing of 0.217 nm consistent with the 111 plane of the catalyst supporting the synthesis of Ni_3FeN nanocatalyst.

Some specific procedures include 1-methylimidazole (1-MD)-fixation" strategy to support nano/micro-sized nitrides on carbon materials [15]. Covalent organic frameworks (COFs) were utilized to support Ni_3N nanoparticles through a solid state synthesis to prepare COF-Ni_3N composite [16]. This approach has two advantages, the first one is, this procedure allows nanoscale confinement of the metal nitride catalyst which is otherwise difficult to achieve. The second advantage is a π-conjugated support further aids the conductivity of nitride catalyst, a property desirable for OER. Though, volatile source rich with nitrogen is treated at high temperature with metal oxides with a programmed temperature ramp is an established procedure to generate the corresponding metal nitrides, plasma treatment is also used in literature to convert $Ni(OH)_2$ to corresponding nitride [17]. This procedure allows the synthesis of catalyst at a relatively low temperature of 250°C using N_2-H_2 plasma as the source. In the above work, Li et al. utilized the plasma treatment to synthesize Ni_3N nanocatalysts of 30 nm size. The XPS and XRD spectra revealed quantitative conversion of the hydroxides to nitrides in a fairly short duration of 1 h. Nitrates [$Ni(NO_3)_2$] can also be utilized as a source to prepare the nitride catalyst as reported in literature. For example, recently a mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ is treated with NH_3 as the "N" source to synthesize ammonium nickel molybdate [18]. The XRD data of the resulting catalyst $NiMo_4N_5$ revealed 111 plane accountable to the FCC lattice of Ni, whereas the planes for crystalline phase related to Mo was absent suggesting uniform distribution of the two metals. Derivation of catalyst from a rigid MOF precursor is recently utilized to develop catalyst with controlled nanostructure. For example, Co-Mo_2N was synthesized by heat treatment of ZIF-67/Mo-MOFs-2 at 500°C for 3 h. The resulting catalyst mimicked the shape of MOF precursor [19]. The XPS data showed the peaks assigned to Mo and N present in Mo-N linkage supporting the synthesis of catalyst.

In most of the synthesis, it has been observed that the shape of the precursor material is retained after nitridation in presence of NH_3 at high temperature. In some cases, the nitridation also induces porosity in the samples. For example, Co_3FeN_x porous nanowires were synthesized from Co_3Fe double hydroxide nanofibers using NH_3 as the nitrogen source at 623 K [20]. The resulting catalysts were effective against both OER and HER and current density values of 20 mA/cm^2 and 10 mA/cm^2 were achievable at 222 mV and 23 mV overpotentials for OER and HER respectively. Sometimes color can be used as an indicator of the surface coating and functional group conversion. For example, $NiFe(OH)_x$ was grown in-situ on bare Ni

foam and the color changed from gray to brown. Further the sample was calcined in presence of NH_3 to convert the hydroxides to corresponding nitrides. The color of the surface changed to black suggesting the functional group conversion [21]. In this case, the Ni foam not only serves as a substrate but also acts as a precursor during the hydroxide growth process via redox itching of Fe precursor. A distinct shift in the Ni binding energy from 853 to 855.7 eV was observed in the XPS spectra suggesting conversion of hydroxides (Ni-OH) to the corresponding nitrides (Ni-N). Recently, a non-stoichiometric NiN_x was directly synthesized from Ni foam by plasma treatment. A piece of Ni foam was exposed to N_2 plasma initiated by microwave for in-situ growth of nickel nitride nanostructures. The SEM and TEM images displayed change in surface morphology after exposure to plasma. The XPS data displayed a peak at 398 eV accountable to the "N" of Ni-N linkage supporting the formation of nanocatalyst on surface of Ni foam [22].

One of the problems that researchers have frequently faced is the weak bonding between the substrate and nanocatalyst. To address this, a strategy was recently utilized via use of inks. Importantly, the strategy worked with a number of metal catalysts and the method was relatively convenient. In this approach, the metal salts were dissolved in an organic solvent to prepare the ink. Subsequently, the substrate was dipped in the ink to soak the salt on the surface. The sample was then heated at 500°C under NH_3 for nitridation. The strategy allowed uniform distribution of the catalyst on surface and the durability of the system was adequate, which will be discussed in the subsequent section. Another challenging aspect of catalyst synthesis is to have a nanocomposite coating of two elements on the metal surface. For example, polymerization-pyrolysis-evaporation strategy was utilized to synthesize nitride doped porous carbon anchored on atomically dispersed FeN_4. The synthetic strategy involved two steps; in the first step bimetallic Zn/Fe polyphthalocyanine was synthesized and in the second step the above polymer was pyrolyzed to produce the final catalyst. The HAADF-STEM data revealed uniform distribution of C and N on Fe surface. The catalytic sites were further demonstrated by [57]Fe Mössbauer transmission spectra [23]. Sputtering technique is also used in literature to deposit metal nitrides on base material such as carbon black and Ni foam. The temperature of the sputtering chamber controlled the stoichiometry of the resulting catalyst. For example, at 90°C Ni_4N was synthesized, whereas at 180°C Ni_3N formed on the surface of carbon cloth at 18 mTorr. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy revealed the bands for both Ni_4N and Ni_3N supporting the stoichiometric control in the above synthesis. Some other specific modes of synthesis of metal nitrides is by utilizing a reactive ammonia species to decrease the reaction temperature. For example, the manganese and iron oxide were treated with $NaNH_2$ to synthesize the corresponding metal nitrides at 240°C [24].

4. Catalytic efficiency of metal nitride based catalysts

Overall, the literature supported that nitrides are more conductive compared to that of the oxides. Owing to the above, metal nitrides exhibit lower overpotential compared to that of the oxides and may be used as bifunctional catalysts for both HER and OER. Doping improves the stability and in some cases the efficiency of the catalyst. Metal alloy can be advantageous as base material. Ni, Fe, Co, Mo are some of the possible low cost metal precursors for utilization as catalyst. Shape of the nanocatalyst also offer possibility of further efficiency improvement. Thin coating of metal nitrides is advantageous compared to the bulk coating. For example, Ni_3N nanosheets exhibited an overpotential value of ~380 mV at 100 mA/cm^2 current density, whereas the bulk sample and the corresponding oxide exhibited

overpotential value of 600 mV to achieve the above current density. The Tafel slope value for the nanosheet was 45 mV/dec, whereas the bulk catalyst exhibited a Tafel slope value of 85 mV/dec. [25] Recently, a $CuNi_2N$ fabricated on carbon cloth, exhibited 71.4 mV overpotential during HER with a Tafel slope value of 106.5 mV/dec. Long time stability test showed the retention of voltage at 10 mV/cm^2 current density for 60 h [26]. A plasma transformed Ni_3N porous nanosheet exhibited 46 mV/dec of Tafel slope value during HER with overpotential marginally higher than that of the Pt/C [27].

Among the metal nitrides studied, ternary metal nitride systems are the most promising, since the coordination number is close to one and the adsorption free energy is close to zero that is most favorable for HER as per the Sabatier's principle [28]. In fact, a large number of ternary metal nitrides have shown high activity towards HER such as NiMo-N [29, 30], CuNi-N [31], CoMo-N [32], Fe_2Ni_2N [33], ZCo_3FeN [34], $NiCo_2N$ [35] and Ni_3FeN [36] Among the non-noble metal systems, Ni-Fe based nitride systems with metallic characteristics, strong absorption of water molecule and unique electronic structure have displayed efficiency towards both HER and OER reaction. Especially, Ni rich compositions have shown promise towards full water splitting. For example, Ni_3Fe-N and Ni2Fe2-N have shown efficiency towards HER and OER [37–40]. Morphology of the catalyst and contact with the GC electrode can significantly affect its performance and long term stability. Therefore, in-situ growth is given importance in the later stage of catalyst development. Especially with the Ni based system, Ni foam could serve as one of the most appropriate base electrode since the contact becomes more efficient. Stacking of multiple electrodes can also be utilized to further aid the efficiency. Overall, the literature has shown that effective catalyst systems based on Ni-Fe/Co-N based systems can be formulated and fabricated for overall electrolysis at low overpotential. The Ni based system is able to yield current density value of 100 mA/cm^2 at a low overpotential of 100 mV along with superior durability. The already formidable HER activity of Ni based system may be further augured by decorating the catalyst with Pt and further improve the current density to 200 mA/cm^2 at 160 mV overpotential [41]. The Co based system are reported to exhibit low activity towards HER since the d band is far from the centre of HER energy level. Though this can be circumvented to some extent by doping with vanadium [42]. Bimetallic systems have invariably demonstrated superior catalytic activities compared to that of their monometallic analog. For example, Ni-Fe [43–45], Ni-Co [46, 47], and Co-Fe nitrides [48] have all exhibited improved catalytic activities compared to that of their monometallic counterparts. Ni_3FeN catalyst materials are one of the leading candidates for use as HER electrocatalysts. Though the mechanism for HER on these nitride surfaces are a matter of intense research, several studies have supported the metallic nature of the catalyst for swift electron transfer necessary for HER. The surface of metal or the "N" that acts as an active centre is still under investigation. OER being a more energy intensive process compared to that of the HER, is more facilitated, when conductive metal nitrides are used instead of oxides. The ratio of metal and "N" influences the electrical conductivity, which subsequently affects the OER efficiency. It was proved in a Co based system (Co_2N, Co_3N and Co_4N) that, increase in Co amount increases the intrinsic conductivity [49].

Nitrides based on other metals such as Mo and Co have shown activity towards either HER or OER. For example, the binary nitride based on Mo_2N showed adequate HER catalytic activity. A composite of Mo_2N-Mo_2C showed enhanced HER activity compared to that of the Mo_2N alone [50]. Similarly, layered conjugation of MoS_2 with MoN_2 also improved the electrocatalytic activity [51]. Direct growth of Mo_2N on CNT and N doped carbon matrix can be utilized to improve the electrocatalytic activity [52, 53], Recently, Mo_2N–Mo_2C heterojunction on the

reduced graphene oxide displayed superior HER activity with low onset potentials of 18 mV under basic medium, that is superior to Pt/C electrode in alkaline media at large current densities [54]. In general, it has been observed that Metal-NC system exhibits superior activity compared to that of the metal nitrides only. Just recently, nitride MXene (V-$Ti_4N_3T_x$) based systems have shown superior HER activity [55]. Several specific examples are discussed below to obtain a fair idea about the catalytic activity of such systems.

Recently, Cai and coworkers have synthesized a Ru cluster of ~1 nm size anchored on N doped carbon surface using a one pot procedure [56]. The resulting catalyst displayed activity towards both HER and OER in alkaline (1 M KOH) medium. Importantly, the over-potential values were notably less in case of both the reactions (HER: 15 mV vs. RHE and OER: 285 mV vs. RHE). The durability test showed that the activity remained largely unaffected after 5000 cycles. They hypothesized that the presence of "N" in the catalyst matrix improved the stability and promoted the HER and OER activity. Similarly, Wu and coworkers have immobilized $Co_{5.47}N$ nanoparticles on C-N matrix by utilizing Co based Zeolite framework as the starting material [57]. The frameworks were pyrolyzed at 700°C in presence of NH_3 to form the CN nanoparticles in-situ. The catalyst system was effective for both HER and OER and the over-potential values (149 mV for HER and 248 mV for OER) were lower compared to that of the IrO_2 benchmark. The catalyst retained ~82% of original current density at an overpotential value of 248 mV after 10 h, which is superior compared to that of the benchmark (56%). The efficiency of nitrides in other cost effective metal systems were analyzed. Catalysts based on Ni_3N nanosheet exhibited adequate OER performance in an alkaline solution and achieved 52.3 mA cm^{-2} current density at relatively low over-potential (350 mV) with small Tafel slope [58]. The nanosheets were prepared by coating an activated carbon cloth with Ni salts and heating the salt coated carbon cloth at 380°C in presence of NH_3. The catalyst also exhibited Tafel slope value up to 45 mV/dec.

The Fe based catalyst (Fe_3N/Fe_4N) nanoporous film on a conducting Ni-graphene foam displayed low OER overpotential (238 mV) corresponding to current density of 10 mA/cm^2 and a low Tafel slope value of 44.5 mV/dec along with high 96.7% faradaic yield. These numbers were superior compared to that of the benchmark IrO_2 and attributed to high electron transfer and surface area of the catalyst [59]. The OER overpotential of the nitrides were far superior than the corresponding oxide as shown below. In fact, a similar trend was noticed with Co based nitride (Co_4N) catalyst system. In which a current density value of 10 mA/cm^2 was achieved at an overpotential of 257 mV with small Tafel slope [60]. Most of the reports on nitride based system revealed the bi-functional nature of the catalyst. These catalysts were effective against both HER and OER under basic conditions. Additionally, most of the catalyst based on the nitrides displayed lower overpotential value compared to that of the oxide based systems. The lower overpotential values of these systems were assigned to their higher conductivity values that resulted from the metallic character arising out of the overlap between Ni-3d and N-2p orbitals in the catalysts. The second promising aspect was their bifunctional behavior, that resulted from the tendency of "N" to donate electron more easily compared to that of the "O" and polarization associated with the shift of "H" from "O" to "N", a key step during HER [61]. The adsorption energy value of "H" on nitride based catalyst system was much lower compared to that of the H_2O and similar to that of the Pt-C bench mark that facilitated the rate of HER. The nitride systems based on the metal alloys exhibited lower overpotential values compared to that of their single metal counterparts. For example, the overpotential value of CoFe(3:1)-N was ~150 mV lower compared to that of the Co-N or Fe-N for OER. The Tafel slope value was approximately 3 times lower in case of alloy

nitrides further supporting the efficiency of these systems towards OER. The ratio between the two metals in the alloy played an important role, while determining the catalytic efficiency [62]. The stability of these catalysts were also excellent as only 4.5% decrease in efficiency was noticed after 10 h of OER. The spatial arrangement of these alloy nitride nanostructures on the base electrode also displayed a variation in catalytic efficiency. For example, NiFe-N grown on Z plane from the electrode surface displayed 277 mV overpotential at 100 mV/cm^2 current density and 337 mV at 500 mV/cm^2, which was lower compared to that of the IrO$_2$ benchmark (542 mV at 500 mV/cm^2) [63]. The Tafel slope value for the above catalyst system was 58.6 mV/dec.

Further studies have shown that, the shape of the nanocatalyst controls the efficiency to a substantial extent. Report based on Rh nanocrystals have shown that, the benzoid structures exhibited lower overpotential in both OER and HER compared to that of the tetrahedral structures [64]. However, the deviation was within 100 mV in case of OER. Interestingly, the Tafel slope value displayed a strong improvement on optimization of the shape. The value for the benzoid structure was 87 mV/dec, whereas the value for the tetrahedral structure was 205 mV/dec. Other factors such as doping of metal nanoparticles on the catalyst can also be used as a procedure to further improve the overpotential value and dependency of current on the overpotential. Recently, a cobalt nitride based nanofiber system was doped with Ir nanoparticle. The resulting catalyst exhibited much lower Tafel slope value compared to that of the undoped system. The overpotential value of the doped system was also lower compared to that of the base nitride system [65]. Similarly, a chromium doped Co-N system exhibited a Tafel slope value of 38.1 mV/dec and retained current density up to 200 h [66]. The system displayed an overpotential value of 99 mV at 100 mV/cm^2. The current versus potential curve was superimposable

Catalyst Composition	Electrolyte Used	Overpotential (mV) @ 10 mA cm^{-2} Current Density	Tafel Slope (mV dec^{-1})	Reference
Ni$_3$N$_{1-x}$/NF	1.0 M KOH	55	54	[68]
Ni$_3$FeN/NF		75	98	[69]
Ni$_3$FeN		158	42	[70]
NiMoN/CC		109	95	[71]
MoON/CC		146	101	[55]
Ni$_3$N/CC		208	113	[55]
Mo$_2$N		353	108	[72]
Ni$_3$N		96	120	[73]
Ni$_3$N/NF		121	109	[74]
NiCoN nanowires		145	105.2	[75]
CoN nanowires		97	93.9	[76]
Co$_{5.47}$N@N-C		149	86	[77]
Ni$_3$N nanorods		305	197.5	[78]
Co-Ni$_3$N nanorods		194	156	[62]
Ni$_3$N nanosphere		185	—	[79]

Table 2.
The table summarizes the values of the overpotential and Tafel slope values for different catalyst compositions. Ref. [67] (supporting information).

after 1000 cycles. The values were superior compared that of the Pt benchmark. A common study involving various earth abundant metal catalysts revealed that Tafel slope value of the non-stoichiometric nickel nitride catalyst coated on Ni (Ni_3N_x) foam is the lowest among various catalyst systems studied (**Table 2**).

5. Durability of metal nitride based catalysts

Published literature provides a fair idea about the durability of nitride based catalysts under electrolysis conditions [80]. We are revisiting several compositions and their lifetime in the following section. The NiMoN nanotube displayed OER efficiency equivalent to that of the IrO_2 reference, as the current versus potential curve almost superimposed in both the cases. The catalyst displayed an overpotential of 295 mV at 10 mA/cm^2 current density. The stability was checked by performing 1000 cycles of CV scanning within 1.036 to 1.636 V at a scan rate of 50 mV/sec. The CV traces remained unchanged after 1000 cycles supporting the stability of nanocatalyst. The stability curve at 295 mV overpotential also retained the current density up to 20 h [30]. The stability comparison between monometallic and bimetallic metal nitrides revealed that later is more stable under HER condition. For example, the CoN under constant overpotential of 100 mV retained current density up to 24 h. The $NiCo_2N$ exhibited current retention up to 48 h under HER condition at lower overpotential (50 mV). The overpotential values of the bimetallic system was also superior compared to that of the single metal system. The electrolysis was carried out under basic conditions (1 M KOH). These enhanced activity is attributed to the synergistic effect of both the metals that increased the conductivity and facilitated the charge transfer necessary for efficient HER [81]. The iron nickel alloy nitride systems have shown most comfortable overpotentials towards OER as described in the previous section. The stability of these class of catalysts becomes important as the plan is to pursue similar composition for our approach. Successive OER and HER was carried out with the same catalyst for 30 h each at an overpotential of 100 and − 100 mV respectively. The sample exhibited adequate stability and the crystallinity also remained intact after the reactions as displayed from the XRD. The durability test also revealed that the current was maintained up to 400 h under basic conditions at 10 mA/cm^2 [21]. A Ru nitride (non-stoichiometric) coated on carbon black catalyst retained current density (10 mA/cm2) up to 50 h, even though the electrolyte was changed two times in between the period. At the same time, the reference could sustain the current only for 10 h and the current density started decreasing to 1 mA/cm^2 after 2 h. Importantly, the chronoamperometry trace was identical to the original one after 50 h of catalysis supporting stability. Similarly, the overpotential value remained intact after 1000 cycles of LSV, whereas the catalyst without nitride coating degraded with a much higher overpotential [82]. An electrolysis study with Co_2N, Co_3N and Co_4N showed that all three catalyst systems exhibited current retention up to 3.3 h at 437 mV overpotential in 0.1 M KOH. The oxygen production value was similar to that of the theoretically calculated value for 1 h. The stability of Co based system was lower compared to that of the Ni/Fe based system. The chronoamperometry trace after 1000 cycle matched with that of the initial one. Overall, Ni in conjugation with other transition metals in the nitride form have exhibited adequate stability with a low overpotential [83]. The overpotential of Ni_3Fe was marginally lower than that of the Ni_3Co nitride and much lower than that of the Ni_3Mn nitride. Both Ni_3FeN and Ni_3CoN exhibited retention of potential (1.55 V) under 100 A/g current density. However, the Ni_3MnN could sustain the activity up to 16 h under OER conditions. The Ni_3FeN exhibited stability under HER conditions with efficiency. The LSV curves were

Catalyst	Morphology	Overpotential (mV)	Onset Potential (V vs. RHE)	Tafel Slope (mV dec^{-1})	Stability
Ni_3N	2D-sheets	250	1.55	45	Excellent
Ni_3N/CC	3D-sheets	190	1.36	112	Good
Ni_3N/NF	3D-sheets	50	1.39	60	Excellent
Fe_2Ni_2N/CNT	1D-sheets	282	1.47	38	Good
Ni_3FeN	2D-sheets	300	1.35	51	Excellent
Ni_3FeN/NW	3D-sheets	200	1.34	40	Excellent
Ni_3FeN/CC	3D-sheets	240	1.45	59	Excellent
Ni_3FeN/CC	3D-sheets	105	1.33	72	Excellent
Ni_3FeN/rGO	3D-sheets	280	1.42	90	Good
$NiCoN/NW$	1D-nanowires	360	1.53	45	Good
Ni_3CoN	2D-sheets	340	1.52	55	Excellent
$NiCo_2N/NF$	3D-sheets	180	1.35	69	Good
Ni_3MnN	2D-sheets	320	1.60	64	Excellent
$NiMoN/CF$	1D-nanofibres	210	1.32	55	Good
$NiMoN/NF$	3D-foams	218	1.35	55	Excellent

The electrolytes used in above cases were 1.0 M KOH or NaOH.

Table 3.
Ni based nitride catalyst efficiency and stability under OER conditions (reproduced with permission from ref. [5] copyright 2019 WILEY-VCH Verlag GmbH).

repeatable after 1000 cycles [84]. Finally, a summary of the Ni based nitride catalyst efficiency under OER condition is presented to obtain a generic understanding about the capability of these class of materials. The overpotential value is distributed within 50 to 360 mV for OER under basic conditions with stability is termed as good to excellent suggesting the chances of developing a Ni nitride based catalyst for commercial grade electrolysis is fairly high (**Table 3**).

6. Effect of salt on electrolysis efficiency

Though most of the articles have studied pure water electrolysis using metal nitrides as the catalyst, a few reports suggests that metal nitrides are promising as the catalyst for sea water electrolysis due to their corrosion resistant and electrically conductive properties [85]. The overpotential values marginally increased, when NaCl was added to the water or seawater was directly used as the electrolyte. In case of NiMoN, the overpotential values increased from 130 to 160 mV, when seawater replaced the pure water as the electrolyte. Interestingly, addition of NaCl to the solution, didn't change the HER overpotential value significantly at 500 mA/cm^2 current density. Similarly, the OER overpotential value increased from 340 to 355 mV at 500 mA/cm^2 current density in presence of salt and the value further increased to 365 mV in presence of sea water suggesting, though the salt water affects the overpotential, the increase is not that significant. The durability tests were also conducted in presence of NaCl and sea water. The overpotential value exhibited minor increase after 100 h at 500 mA/cm^2 current density suggesting the catalyst may be a viable option for exploring possibility as a commercial catalyst towards further research and development [63]. Recently, a Mo_5N_6 nanosheet along
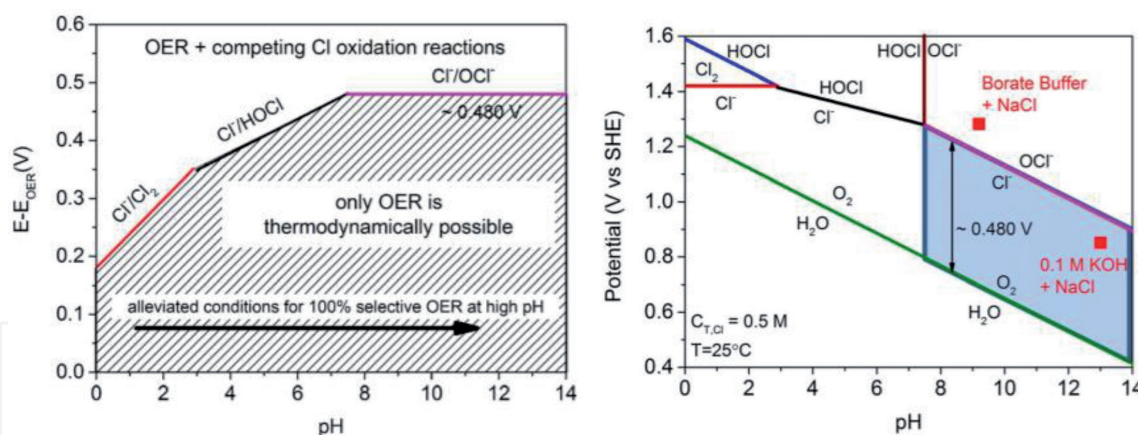
Figure 1.
The overpotential versus pH for the selective OER and the form of Cl⁻ conversion in presence different pH conditions (reproduced with permission from ref. [3] copyright 2016 WILEY-VCH Verlag GmbH).

with several metal nitrides were studied for their efficiency towards sea water electrolysis. As per the report, the HER overpotential was least affected by the presence of sea water. Similarly, the current retention was also 100% after a 100 h cycle at an applied potential of 310 mV [86]. Similarly, a NiNS based bifunctional catalyst system was also studied for sea water electrolysis. A current density value of 48.3 mAcm^{-2} at 1.8 V was achieved for overall sea water electrolysis. The current density value marginally decreased from 15 to 13 mA/cm^2 over 12 h period of electrolysis. To conclude, the overpotential values associated with these metal nitrides based catalyst systems are adequate to carry out electrolysis without affecting Cl⁻ ion. In case of basic pH electrolysis, the allowed overpotential is 450 mV, whereas under acidic conditions, the overpotential is limited to ~250 mV. Moreover, the Cl⁻ is expected to release as Cl$_2$ gas under acidic conditions, whereas under basic conditions, the hypochlorate ion is going to precipitate as salt and may not affect the efficiency to a certain extent (**Figure 1**). Therefore, considering the overall scenario, basic electrolysis system may be one of the safer option when sea water is a part of the electrolyte.

7. Conclusions

In conclusion, the chapter enlightens the necessities of nitride based catalysts for sea and ground water electrolysis in the preliminary section. Subsequently, the synthetic strategy utilized for these metal nitride nanocatalysts, their efficiency and efficacy in presence of sea water as electrolyte is summarized. To ensure H$_2$ energy becomes one of the commercially viable energy source for consumption, a sustainable generation mode is highly desirable. Metal nitride based catalysts have shown promise to fulfill the same with numerous research publications providing scientific data in support of the above. Though, still commercial implementation is yet to be achieved with these class of catalyst materials, we can safely assume that in near future a realistic design of electrolyzers possessing these nitride nanocatalyst modified electrodes may be available for commercial production.

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