Green chemistry approach for a greener hydrogen production cycle and water oxidation

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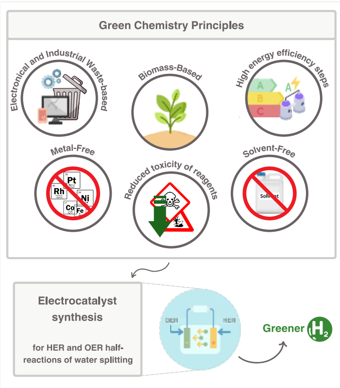

Despite the green perspective of water electrolysis, the synthesis of electrocatalysts is heavily connected to waste generation and environmental impacts during the whole processing cycle, from the choice of reagents to the disposal of the electrocatalyst. Of various transition metal (TM) oxides/(oxy)hydroxides, spinel-type oxides (AB_2O_4) have been investigated extensively and exhibited outstanding performance towards water oxidation reaction due to their low cost and high stability. However, several other studies have been developing materials for HER and OER application through green chemistry approaches to reduce the synthesis impact. In this work, different strategies from the literature towards green chemistry are discussed, such as the use of biomass as carbon source, industrial and electronical waste as metal sources, solvent-free and metal-free procedures, as well as applying treatment steps that rely on lower energy consumption.

Introduction

By 2023, the GISTEMP database from NASA reported an increase of 1.25 °C on the global average temperature of Earth since the pre-industrial revolution period [1]. This temperature rise is associated with greenhouse gas emissions by human activity, such as carbon dioxide and methane, mainly due to fossil fuel burning for energy generation [2]. In order to hinder this warming tendency and not crossing the 1.5 °C limit of global average increase from the Paris Agreement, extensive changes must be done in every economic sector, especially on the energy source structure, which is deeply dependent on fossil fuels.

The leading pathway for green hydrogen production regarding the current industrial scalability is the water electrolysis. The overall reaction is essentially divided in two half-reactions occurring on each electrode, the hydrogen evolution reaction (HER) at the cathode, and the oxygen evolution reaction (OER) at the anode, involving the water oxidation and reduction. Due to the high stability of the water molecule, both reactions are not spontaneous ($\Delta G > 0$) and have sluggish kinetics.

In this regard, the use of electrocatalysts is indispensable to minimize the required electricity input. One of the most commercialized electrolyzer technologies (PEM, polymer electrolyte membrane) is still based on noble metal electrocatalysts, such as Pt for the cathode (HER) and Ir/Ru oxides for the anode (OER). Despite possessing the most efficient electrocatalytic activities towards HER and OER, their exorbitant cost and scarce availability inhibit the green hydrogen potential [3]. Therefore, efforts have been done to elaborate noble metal-free electrocatalysts, using earth-abundant transition metals (mainly Ni, Co, Fe, Cu, Mo) and their alloys.

However, as the ongoing requirements are to disrupt the pollution cycle and to promote sustainable and greener processes, simply working with earth-abundant and low-cost materials in chemical syntheses is not enough, it is important to consider the entire course of the process. In the case of electrocatalysts, the processing of transition metals commonly involves the use of hazardous chemicals, low energy efficient steps, and the generation of toxic wastes during its whole life cycle, from the metal mining to the electrocatalyst disposal. In this way, it is essential to propose ecological routes by applying green chemistry approaches envisioning the whole procedure and estimating the impacts of the process.

The green chemistry concept was firstly introduced in 1991, which was then consolidated in 1998 [4]. Several metrics were then created to assess how green a process is, such as atom economy, environmental factor (E-factor), life cycle analysis (LCA), EcoScale, and others [5].

In this study, an overview of electrocatalysts synthesis routes for HER and OER with a green chemistry approach is provided, promoting a discussion on the pollution at source and waste generation. The goal is to stimulate the succeeding studies to evaluate the impacts of the designed synthesis through at least one of the green chemistry metrics.

State of the Art

A metal-free biomass-based electrocatalyst was obtained by Kumaresan *et al*. (2023) through the carbonization of *Acorus Calamus* (also known as sweet flag) after HCl washing, applying a step heating of 200 °C (12 h), 450 °C (4 h) and 750 °C (4 h) under N_2 atmosphere, with milling treatment using KOH pellets before the last heating step [6]. The high surface area (3488 $m^2 \cdot g^{-1}$) nitrogen-doped carbon nanosheets electrocatalyst was tested for both HER and OER applications, obtaining respectively -330 mV and 563 mV vs. RHE as overpotentials at -10 and 10 $mA \cdot cm^{-2}$ of current density. The electrocatalyst displayed almost zero degradation after 10 h of measurement, showing excellent stability for the application. The overall synthesis procedure is simple, with small number of reagents (biomass, HCl and KOH), in addition to being solvent and metal-free. The absence of metallic compounds can be interesting from the environmental point of view, since several steps with elevated potential of pollution generation are avoided. However, its overpotentials were not as efficient as the metal-based electrocatalysts.

Pitchai *et al*. (2024) also synthesized a biomass-based electrocatalyst for HER from *Luffa acutangular* (ridge gourd), however a metal source was added in this synthesis. A better activity towards HER ($\eta_{@10}$ = -173 mV) was obtained for this electrocatalyst. The nickel sulfide modified nitrogen-doped carbon dots catalyst (α-NiS@NDCD) was produced using a more energy efficient process: a two-step hydrothermal reaction at 180 ºC (12 h) and 120 ºC (6 h) [7]. However, the authors added some toxic compounds in the synthesis procedure, e.g. (i) a metal source, nickel nitrate, and (ii) a sulfur source, thiourea, which are both CMR substances (carcinogenic, mutagenic and/or reprotoxic) and can impact the aquatic life with long lasting effects.

Although the absence of metals in the electrocatalysts synthesis is an engaging approach, the advantages of the electronic structure of metals are well known in the literature [8]. Therefore, exploring routes that introduce metals from metallic wastes are of utmost importance. In this regard, Gomaa *et al*. (2022) developed an electrocatalyst made of annealed and anodized stainless steel (SS 316L) meshes obtained from construction sites waste [9]. The anodization was performed by submerging the SS mesh for 5 min in a bath of 70 % ethylene glycol, 5 % sulfuric acid, 5 % water, 20 % methanol and 3 M ammonium fluoride, at 40 V. After anodization, the meshes were annealed at 450 ºC (1 h) under O_2 atmosphere. The overpotential of 280 mV towards OER at current density of 10 $mA{\cdot}cm^{-2}$ was observed for the modified mesh ($\eta_{@10}$ = 400 mV for the mesh without treatment). This route developed an efficient OER electrocatalyst from industrial waste of stainless steel, employing a low energy consumption processing step. Although the anodizing bath employed hazardous compounds such as methanol, ethylene glycol and ammonium fluoride, this bath could be reused and then treated after losing its capacity.

Developing new HER and OER electrocatalysts based on green chemistry principles requires extensive research to establish green synthesis routes and reagents, for later transferring such technologies to the industry. In addition, a standardized evaluation method should be applied for each study, in order to allow a fair comparison between electrocatalysts synthesis routes. Nevertheless, rare are the research papers which apply any green chemistry metric.

Conclusions

Although the hydrogen cycle as a fuel is the greenest when it comes to electrolysis of water from renewable energies, the synthesis of electrocatalysts is still intrinsically linked to environmental impacts. Thus, implementing green chemistry approaches is crucial to develop low-pollution and environmentally-safe routes for HER and OER electrocatalysts. The ongoing research efforts for HER and OER electrocatalyst synthesis are focused on some strategies discussed in this work, such as exchanging toxic reagents to lower toxicity levels, employing solvent and metal-free routes, applying higher energy-efficiency steps, employing biomass and wastes from industry and electronics, and other strategies. However, none of the studies for HER or OER electrocatalysts applied any green chemistry metric to assess its synthesis procedure, hindering comparisons and thus to achieve an effective and low-impact pathway for a greener hydrogen cycle.

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