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Review article

Recent advances in hydrogen evolution reaction catalysts on carbon/carbon-based supports in acid media

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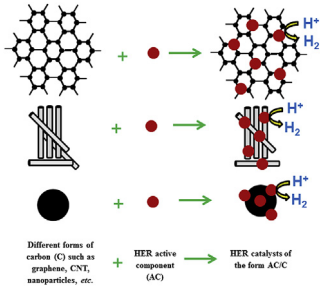
HIGHLIGHTS

- Significance of HER in the context of present energy crisis is discussed in detail.
- The review examines catalysts of the form AC/C (AC = active component, C = carbon).
- Carbon support aids AC by providing high surface area and conductivity.
- The contribution of carbon in the enhancement of HER activity is highlighted.
- Electrochemical parameters of the catalysts AC and AC/C are compared and discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The present and future energy demands of burgeoning global population require an energy currency that can be obtained from clean and renewable resources. In this context, hydrogen as the future energy currency is widely considered as the solution to the energy crisis. Efficient electrocatalysis of hydrogen evolution reaction by inexpensive, highly active, abundant, environmental friendly and stable electrocatalyst is vital for the low-cost production of hydrogen. Carbon as the hydrogen evolution reaction catalyst support is explored since the initial period of the United States space program. The importance of carbon as the support material is understood by the fact that hydrogen evolution reaction electrocatalysis demands not only efficient electron transfer at its surface but also effective electron transport within the electrocatalyst. The hydrogen evolution reaction electrocatalysts presented in this review specifically have two components: 1) hydrogen evolution reaction active component and 2) carbon or carbon-based support for the active component. However, when carbon supports are coupled with the hydrogen evolution reaction active materials, the activity of these materials is enhanced significantly. The contribution of carbon support in the enhancement of the catalytic activity is discussed and highlighted by comparing the electrochemical parameters of supported and unsupported electrocatalysts where available.

1. Introduction

Energy crisis is one of the most important and pressing topic of discussion world over mostly arising from an ever expanding gap between energy demands of burgeoning global population and its supply [1,2]. It has been predicted that the continuation of fossil fuel based

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industrial civilization will result in a collapse the same rather sooner than later [3]. Carbon dioxide (CO_2) from fossil fuel combustion is being added to the atmosphere at an alarming rate that increase in global temperature is already evident [4,5]. The rise in global temperature would lead to melting of polar ice and consequently rise in sea level that would immerse low-lying/coastal cities. Moreover, fossil fuels such as coal contain sulfur and releasing sulfur into the atmosphere because of fossil fuel usage results in sulfurous fogs and acid rains in the industrial cities. Environment pollution due to fossil fuel combustion further complicates the problem of fast dwindling available fossil fuel.

It is being intensively discussed world over politically to limit the fossil fuel usage and hence CO_2 emission. Alternative clean energy sources, especially renewable sources, are widely acknowledged as the solution to the above crisis and are actively explored [6–12]. Sunlight, being the prime source of renewable energy, is available in plenty especially in the countries of the equator region. However, renewable resources, for example, solar energy are sporadic and intermittent in nature and need to be stored in high energy density source, namely, hydrogen [13–19]. Large-scale energy storage in batteries is not viable because of high cost and low energy density of the batteries [20]. Furthermore, hydrogen can be used for direct conversion of chemical energy into electricity in fuel cells rather than in combustion devices [21]. Hydrogen produced by non-electrochemical steam reforming of natural gas leads to inimical CO_2 as well that will increase the CO_2 content of the atmosphere. Hence, electrocatalytic/photoelectrocatalytic water splitting is the alternative route for hydrogen production without CO_2 emission [22,23]. The cathodic half reaction of the water splitting reaction is hydrogen evolution reaction (HER),

$$2H_3O^+ + 2e^- \leftrightarrows H_2 + H_2O \quad (1)$$

The above reaction occurs at the surface of a catalyst and it takes place at the noble metal platinum (Pt) or Pt based catalysts with the lowest overpotential (η) possible. The highest HER activity of Pt is described based on well-known Sabatier's principle [24] and the present state of the art electrocatalysts for HER are Pt or Pt based electrocatalysts [25–31]. Hence, it is imperative to explore alternative electrocatalysts that are inexpensive, highly active, abundant, environmental friendly and importantly stable enough for long term operations in commercial electrolyzers. There has been extensive growth on the research and development on HER in the past years because of the necessity for alternative green technology. This can be understood from the fact that research publications on HER have been increasing exponentially since the past decade as illustrated in Fig. S1.

The green technology of producing hydrogen from water has not yet reached the commercial level. Hydrogen presently is produced predominantly from natural gas, methane, naphtha, *etc*. Photocatalysis is the simplest way to produce hydrogen from water requiring only three components – water, solar energy and photocatalyst. While water and sunlight are available in abundance, efficiency of the photocatalyst remains as the bottleneck. This is because though photocatalysis appears simple, as described above, water splitting is an endothermic reaction requiring photon energy higher than 1.23 eV [32] involving series of photophysical and electrocatalytic steps [33]. Photocatalysts absorbing solar energy in the visible range with high energy conversion efficiency is essential to further this technology [34]. Photocatalysts with enhanced activity have been synthesized recently by combining transition metal phosphides [35,36] with carbon species like graphitic carbon nitrides [37–39], graphene oxide, *etc*. Water splitting occurs at photoelectrochemical (PEC) device at photoanode and/or photocathode with the aid of external bias. Three major physicochemical processes that take place in a PEC device are – 1) light absorption by semiconducting photoelectrode, 2) Separation and transportation of electron-hole pair and 3) Redox water splitting at the surface of the catalyst. There are several types of PEC device configurations; from simple single semiconducting light absorbers to heterojunction photoelectrodes [40,41].

HER activity of an electrocatalyst depends on effective electron transfer at its surface and efficient electron transport within the catalyst as well; the criterion not met by most non-metallic electrocatalysts because of poor conductivity. For example, molybdenum disulfide (MoS_2) nanoparticles though highly active at its surface suffer from being semiconductor and anisotropic nature that limit the overall HER activity. Tafel slope, an inherent property of an electrocatalyst, increases leading to increasing η, consequently to high production cost of hydrogen. The above bottle neck can be circumvented by incorporating a conducting component such as carbon into the electrocatalyst. The above notion is widely emphasized in the literature, for instance, Hinnemann, et al., showed MoS_2 nanoparticles supported on inert and highly conducting carbon as highly active material for hydrogen evolution [42].

Carbon as the HER catalyst support was explored since the initial period of the US space program [43]. Several allotropes of carbon such as carbon nanotubes (CNT), graphene, fullerenes, carbon nanodots, carbon nanospheres, *etc*. form important components of advanced catalysts for HER. The advantages of these materials in the fabrication of catalytic materials are manifold −1) Carbon materials are abundant, possess strong endurance in acid/base media and their molecular structures can be tuned. 2) Catalytic materials can be grown or deposited on the carbon supports in smaller dimensions (nanoparticles) which otherwise may result in aggregation of the catalysts. Nano sized particles possess inherent advantage of having larger surface area, thereby, abundant active sites. 3) High electronic conduction pathways are provided by the carbon supports between the electrode and the catalyst or semiconductor or molecules, *etc*. 4) Synergetic coupling between the conducting carbon and the catalyst enhances the reaction rate and hence the catalytic activity. 5) Carbon supports being insoluble and stable provide high durability to the catalysts so that a long life, especially, for proton exchange membrane (PEM) based energy related devices can be achieved. 6) In some systems, carbon supports provide directionality of electron transfer, for example, recombination reactions [44]. A judicious fabrication of carbon support incorporating non-noble metals, semiconductors, inexpensive earth-abundant materials results in next-generation advanced catalysts for energy storage and conversion applications [45]. The examples include, Mo_2C/CNT based nanorafts [44], integrated solar energy storage and conversion platform [46], multi-step hydrogen evolution catalysis [47], *etc*. The important objectives of this review are given as follows;

1. The carbon supported HER electrocatalysts reviewed are composed of two components – 1) HER active component (AC) and 2) carbon or carbon-based support (C) for the active component, *viz.* of the general form AC/C. In most cases, the support materials alone have no or negligible HER activity in the explored potential domain.
2. Another important objective of the review is to discuss the enhancement or improvement of HER activity of the carbon supported electrocatalyst with respect to the unsupported active component (AC). The electrochemical parameters of AC/C are compared with unsupported electrocatalyst (AC) where available (Table 1) so as to highlight the contribution of carbon support in the forms of high surface area, superior conductivity, *etc.*, to the electrocatalysis of HER.
3. General protocols and procedures to incorporate carbon materials into the active component will be of immense use to the electrochemists working in HER. Hence the purpose of the review is to provide general synthetic procedures for the incorporation of carbon materials into some important classes of HER electrocatalysts.
4. Electrochemical procedures are to be followed carefully while evaluating activity and other parameters such as Tafel slope of an electrocatalyst. The review is also aimed to discuss briefly on the fundamentals of HER and the pitfalls to be avoided while analyzing an electrocatalyst using electrochemical methods.