The recent progress and future of oxygen reduction reaction catalysis: A review

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ARTICLE INFO

ABSTRACT

Proton Exchange Membrane Fuel Cell (PEMFC) technology is an exciting alternative energy prospect, especially in the field of transportation. PEMFCs are three times as efficient as internal combustion (IC) engines and emit only water as a byproduct. The latter point is especially important in a day and age when climate change is upon us. However, platinum required to catalyze the sluggish oxygen reduction reaction (ORR) which takes place on the cathode of the PEMFC has rendered fuel cell automobiles economically unviable until now. Therefore, the pursuit of an inexpensive replacement for platinum has become an active research area. This review covers the promising progress made in this field since 2011. Some of the more promising catalysts reviewed include alloys such as Pt/Pd nanotubes which outperform their platinum counterpart by nine fold and a Pt/Ni alloy which improves upon Pt activity by 16 times. Platinum-free catalysts such as iron carbide and modified graphene which rival Pt activity are also reviewed.

1. Introduction

Internal combustion (IC) engine based vehicles have served people for over 150 years. Obviously, their contributions to the progress of modern civilization can never be overestimated. However, their detrimental impacts on the environment should not be underestimated either. IC engines are inefficient (15%), and emit harmful pollutants including CO_2, around which much controversy has risen [1–6]. Therefore, it is essential that alternative methods for fueling transportation are pursued. Among these alternatives is proton exchange membrane fuel cell (PEMFC) technology. PEMFC vehicles boast much higher energy efficiencies (50–60%) than IC engines and zero carbon emissions [7].

Many obstacles stand in the way of the commercialization of PEMFC vehicles such as hydrogen production and fueling station infrastructure [8]. However, the high cost of PEMFC vehicles is what keeps them from becoming realistic competitors to IC automobiles. The costliest component of the PEMFC is platinum which catalyzes both the anodic and cathodic reaction. Platinum catalyzes the oxidation of H_2 into protons and electrons on the anode, but the overpotential for this reaction is relatively low necessitating correspondingly low loadings of platinum [9]. However, a much larger loading of platinum is required on the cathode in order to catalyze the sluggish and rate limiting

oxygen reduction reaction (ORR) [10–12].

Obviously, the cost of this platinum catalyst is the main hindrance to mass production of PEMFC vehicles. Indeed, platinum loadings in PEMFCs need to be cut by a factor of ten in order to make PEMFC automobiles economically competitive with their IC counterparts [13,14]. In addition, the limited supply of the precious metal (PM) is not abundant enough to sustain global mass production of fuel cell cars without cost-effective recycling methods [15].

Therefore, a number of studies have been conducted to develop new ORR catalysts which can overcome the abovementioned challenges associated with the use of platinum catalysts. These studies have been focused on two areas: alloying the precious metal with another metal in order to increase the mass activity with respect to platinum (A mg^{-1}-Pt) and, eliminating the need for platinum by producing non-precious metal catalysts that can match platinum in catalytic activity. This review will cover the advances in these fields that have been made in the last five years.
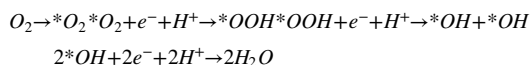
1.1. The reaction

ORR can take place via two pathways. The first, commonly referred to as partial reduction, involves a two electron pathway resulting in the production of adsorbed hydrogen peroxide. Full reduction follows a
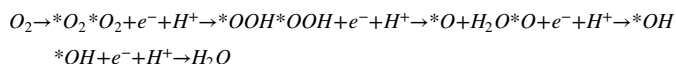
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more efficient four electron pathway which does not involve the production of H_2O_2 [16–18]. Due to the improved efficiency of full reduction as well as the relatively high reactivity of hydrogen peroxide compared to the stability of water, full reduction is the pathway that is sought after when choosing a catalyst for the ORR [19]. For partial reduction to take place, O_2 is first adsorbed on to the catalyst surface. Then, two hydrogen additions take place resulting in an adsorbed H_2O_2 molecule. The hydrogen peroxide product can then undergo further reduction to produce two water molecules, or it can simply dissociate resulting in a free H_2O_2 molecule [18,20]. Full reduction is a dissociative adsorption process which begins with the adsorption of O_2 on the catalyst surface. Following O_2 adsorption, the first electron transfer in the form of hydrogen addition takes place resulting in *OOH. This is followed by the second electron transfer, again in the form of hydrogen addition. Depending on whether this second hydrogen addition takes place at the oxygen molecule adsorbed to the catalyst or if it takes place at the oxygen already bound to the hydrogen determines how the reaction moves forward. If the second hydrogen addition takes place at the oxygen adsorbed to the catalyst (mechanism 1), it results in two adsorbed OH groups. Subsequent electron transfers in the form of hydrogen addition take place at each *OH group resulting in the production of two water molecules. If the second hydrogen addition takes place at the oxygen already bound to the first hydrogen (mechanism 2), this results in desorption of a water molecule and an adsorbed O atom. Two electron transfers in the form of hydrogen addition to the *O follow resulting in desorption of a second water molecule. DFT simulations of the two pathways show that mechanism 1 is thermodynamically favored, and it is therefore the more realistic method [18,20–23].

Mechanism 1

$$O_2 \rightarrow *O_2 \, *O_2 + e^- + H^+ \rightarrow *OOH \, *OOH + e^- + H^+ \rightarrow *OH + *OH$$

$$2*OH + 2e^- + 2H^+ \rightarrow 2H_2O$$

Mechanism 2

$$O_2 \rightarrow *O_2 \, *O_2 + e^- + H^+ \rightarrow *OOH \, *OOH + e^- + H^+ \rightarrow *O + H_2O \, *O + e^- + H^+ \rightarrow *OH$$

$$*OH + e^- + H^+ \rightarrow H_2O$$

1.2. Sustainability

Although the operation of the fuel cell itself produces no harmful emissions, the production of the high purity hydrogen fuel does. This hydrogen production is carried out in a variety of ways, all with their own advantages and disadvantages (Fig. 1)..

Most of the hydrogen production technologies utilize natural gas as a feed stock. Hydrogen is produced from natural gas via steam methane reforming during which methane is reacted with steam to produce CO and H_2. This is followed by the water gas shift reaction which, in the presence of steam, converts the remaining CO to CO_2 and more H_2. Although this process does produce CO_2, it emits none of the harmful NO_x which are emitted by internal combustion engines.

18% of the hydrogen produced around the world is made using coal as a feed stock. This involves the gasification of coal to synthesis gas, mostly CO and H_2. The CO is reacted with steam in the water gas shift reaction to produce more hydrogen and CO_2. Again, hydrogen production via coal results in the production of CO_2 along with other pollutants associated with coal. However, an argument can be made that hydrogen production using coal is more sustainable than using natural gas since coal resources are far more abundant than those of natural gas.

The most environmentally friendly hydrogen production method is electrolysis, which splits water into hydrogen and oxygen gas using electric current. The sustainability of hydrogen production via electrolysis depends on the electricity source. If renewable energy sources
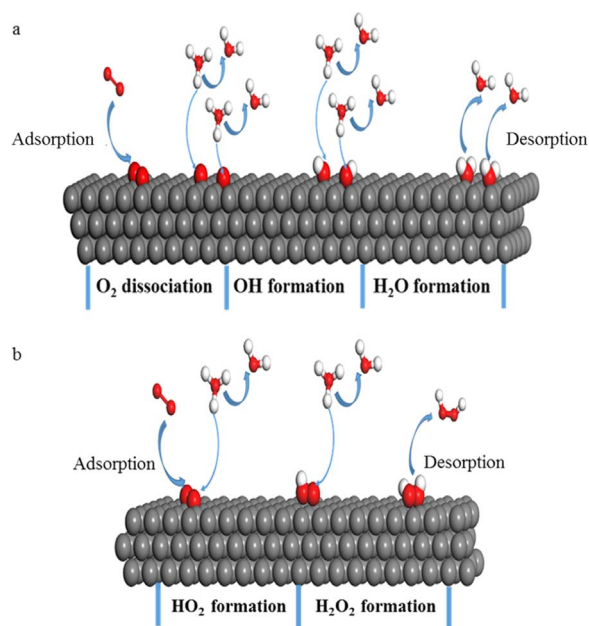

Fig. 1. Mechanism schematics based on the work of Zhang et al. [24] of (a) full reduction and (b) partial reduction of oxygen.

such as solar or wind are used to power electrolysis, PEMFCs can truly be zero emission vehicles.

Regardless of hydrogen production method, the efficiency of PEMFCs makes them sustainable and attractive. These efficiencies translate to 60 mpg on an mpg basis, far outperforming their IC counterparts. So, whatever the feedstock, these efficiencies mean that stock will last longer [25].

1.3. Optimizing ORR catalysts

Density functional theory (DFT) calculations indicate that the binding energy between oxygen intermediates and the catalyst surface is related to catalytic efficiency for ORR [17,26]. The Sabatier principle is the idea that a reactant must bind strongly enough to the catalyst for the reaction to take place, but weakly enough that the product will dissociate and the catalyst surface will not be poisoned by either the reactant or intermediates [27–30]. So, in this case the oxygen species must bind tightly enough to the catalyst that the reaction can take place on the surface, but not so tightly that oxygen intermediates poison the catalyst. Based on both theoretical calculations and experimental data, "volcano plots," like the one seen in Fig. 2, can be constructed comparing catalytic activity to oxygen binding energy (ΔE_O) [23]. These plots can then be used to find the optimal ΔE_O for an ORR catalyst..

Among the catalysts under consideration in Fig. 2, Pt catalysts occupy the most optimal position. However, Pt is not at the peak of the volcano. Therefore, there is room for improvement when designing an ORR catalyst. One method to change adsorption energies of oxygen intermediates is adjusting the center of the d-band, or conductive band, of the catalyst The d-band acts as a descriptor of the electronic properties of the solid, and it has been shown to correlate with adsorption energies [31]. Bimetallic catalysts, specifically core shell arrangements, have been shown to shift the d-band center relative to bulk metals [32,33]. In Section 2.1.1, Kuttiyiel et al. use this d-band/ΔE_O correlation along with a Sabatier style volcano plot in order to optimize the d-band center for their catalyst [34]. Another method for changing the electronics of a catalyst is tuning the predominant facets that are present on the surface [35]. Each crystal plane possesses a specific surface energy, and therefore different binding energies to reactants and different ORR activities [36]. Indeed, Stamenkovic et al.