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Full Length Article

Density functional theory–based design of a Pt-skinned PtNi catalyst for the oxygen reduction reaction in fuel cells

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ABSTRACT

Pt-based binary alloys (Pt-M, M = transition metal) with optimal electronic and geometric properties may be used to secure the economic feasibility of fuel cells by reducing Pt content and increasing cathodic efficiency. Herein, the oxygen reduction reaction (ORR) on Pt-M alloys (Pt_3M and PtM, M = Co, Ni, Mn, and Ir) was probed by density functional theory calculations to reveal that the oxygen dissociation pathway is optimal for Pt(1 1 1), Pt_3M(1 1 1), and PtM(1 1 1) surfaces. However, as the above alloys were inferior to Pt catalysts, Pt/Pt-M alloys were designed by the addition of a single Pt skin layer at the top of Pt-M alloys, which enhanced ORR performance by decreasing the adsorption strengths of key intermediates (O* and OH*) to values below those observed for the Pt catalyst. Pt/PtNi and Pt/PtCo catalysts, which offer the benefit of decreased Pt content, showed particularly high performances. The results of electronic structure analysis demonstrated that the above decrease in adsorption strength was due to the inhibition of the high activity of the Pt-M(1 1 1) surface by the Pt skin layer. Finally, simple descriptors (optimal d-band center position and adsorption strength) were established to enable the further search for better fuel cell catalysts.

1. Introduction

Since the industrial revolution, fossil fuels have been used as energy sources to enable economic growth, scientific and technological progress, and the spread of convenience facilities. However, the unconstrained consumption of fossil fuels causes global climate change and air pollution, thus adversely affecting human health [1]. Among the various ways of mitigating these problems, the development of alternative energy sources (e.g., fuel cells) to reduce fossil fuel usage has drawn much attention [2,3].

As a recognized future energy source, polymer electrolyte membrane fuel cells (PEMFCs) exhibit high power densities and can be stably operated at low temperatures [4,5] but suffer from the limitations imposed by the use of hydrogen as a fuel, e.g., the high cost of building hydrogen fiilling stations [6]. The practical efficiency of fuel cells is most strongly influenced by the energy barrier of the cathode reaction (oxygen reduction reaction (ORR)), while the barrier of the anode reaction (hydrogen oxidation) is much lower [7]. In addition, the commercialization of fuel cells is hindered by the high cost of Pt typically used as the ORR catalyst [8]. For instance, compared to common gasoline vehicles, the currently marketed PEMFC-powered vehicles are 100–200% more expensive, mainly because of the high Pt content of PEMFCs, and are also more costly to maintain in the long term [9].

The above drawbacks have inspired the development of non-Pt-based catalysts (e.g., carbon nanotube- or graphene-based catalysts [10], supported single-atom catalysts [11], and core–shell-structured nanoclusters [12]) with high stability, selectivity, and ORR activity [13]. Despite the significant progress in this field, Pt catalysts are still widely used because of their excellent performance. As alternatives to Pt catalysts, Pt-based binary (Pt-M) alloys offer the benefits of high ORR activity and lower Pt content, thus holding great promise for PEMFCs [14].

Previous works have focused on the use of Pt-M (M = Co [15], Ni [14,16–18], Mn [19], Ir [20,21], or other transition metal [22,23]) binary alloys as fuel cell cathodes and showed that these alloys can exhibit ORR activities exceeding those of pure Pt. In particular, binary alloy catalysts supported by carbon (e.g., graphene) or modified with Pt skin layers were demonstrated to feature enhanced stability and activity [16,24]. However, in this case, unlike for pure metal catalysts, one needs to consider the complex electronic and geometric effects due to variables

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