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First-principles understanding of durable titanium nitride (TiN) electrocatalyst supports

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ABSTRACT

Transition metal nitrides possessing superior electrical conductivity and outstanding oxidation and corrosion resistance have been described as good substitutes for carbon support materials which are vulnerable during proton exchange membrane fuel cell (PEMFC) operation due to corrosion and poor life cycles. A closer theoretical inspection of the stability and electronic properties of titanium nitride-supported Pt in comparison with carbon-supported Pt (using graphite and graphene) has been conducted using density functional theory calculations. A single Pt atom adsorbed more strongly to the TiN surface than to both graphite and graphene, causing a larger degree of charge transfer between Pt and TiN.

Introduction

Stable catalyst support materials are important for improving the durability of proton exchange membrane fuel cell (PEMFC) cathodes. Although fuel cell degradation could be attributed to the collective degradation of its components, the corrosion of carbon support materials during operation is considered one of the main modes of failure that prevents high fuel cell performance [1]. Carbon supports are particularly vulnerable during fuel cell operation in the presence of oxygen at low to zero load during load cycling [2]. Therefore, it is necessary to explore stable alternatives to carbon materials as catalyst supports to improve the durability of PEMFCs.

Recently, transition metal nitrides, some of which also possess catalytic activity similar to those of noble metals like Pd and Pt have been reported as promising catalyst supports [3,4]. Among different metal nitrides, titanium nitride (TiN) seems to be the most attractive candidate because of its superior electrical conductivity and outstanding oxidation and acid corrosion resistance [5–9].

Our recent experimental results [10] and other publications on the subject [11,12] yield clear and compelling experimental evidence of the significant beneficial effects of TiN on supported Pt catalysts in terms of catalytic activity and durability in the oxygen reduction reaction (ORR). This evidence was obtained through comparison with commercially available carbon-supported Pt catalytic systems. For example, initial oxygen reduction performance was revealed to be comparable in both cases, while Pt-TiN showed higher durability than commercial Pt-C. Significantly, unlike carbon-supported Pt, both the morphology and electrochemical behavior of Pt nanoparticles on a TiN support remain unchanged during extended potential cycling.

Besides the experimental work, there are only a few theoretical studies on transition metal nitrides as electrocatalyst supports for PEMFCs [3,13–15]. These have investigated the adsorption behavior of Pt, the electronic properties of Pt and TiN, and various reaction mechanisms of oxygen reduction, formic acid oxidation, and carbon monoxide poisoning. In the current study, we have undertaken a closer inspection of Pt stability and electronic properties by comparing Pt-TiN and Pt-carbon (represented by graphite and graphene), in order to provide insight into the origins of durability in the Pt-TiN system and preparation methods for improving these active catalytic centers.

Computational methodology

Spin-polarized density functional theory calculations were performed by the Vienna *ab initio* Simulation Package (VASP) [16–19] using the projector-augmented wave (PAW) [20,21] method. Electron exchange-correlation functionals were represented with the generalized gradient approximation (GGA), and the model of Perdew, Burke, and Ernzerhof (PBE) [22] was used for

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