



Screening the best catalyst with group 9, 10 and 11 metals monolayer loading on NbC(001) from first-principles study

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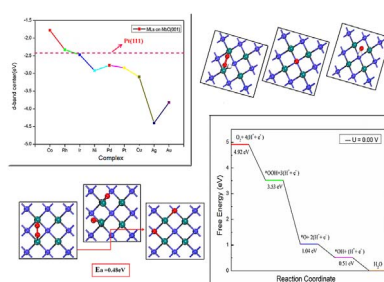
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HIGHLIGHTS

- Four criteria are used to screen the best ORR catalyst of metal ML on NbC(001).
- The properties of group 9–11 metals supported on NbC(001) are studied.
- Pd_{ML}/NbC(001) is determined as an ideal catalyst that meets the criteria.
- Pd_{ML}/NbC(001) is a potential candidate to replace the Pt-based catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

The supported catalysts have received great attentions due to their high catalytic activity, low cost and good stability. Here we report the stability, wetting ability, corrosion resistance and catalytic activity of the supported catalysts with group 9, 10 and 11 metals ($M = \text{Co}, \text{Rh}, \text{Ir}, \text{Ni}, \text{Pd}, \text{Pt}, \text{Cu}, \text{Ag}, \text{Au}$) monolayers (ML) deposited on NbC(001), denoted as $M_{\text{ML}}/\text{NbC}(001)$. The Pd_{ML}/NbC(001) and Pt_{ML}/NbC(001) are testified as the most stable and active ones with the former even better on the whole. The catalytic activities toward oxygen reduction reactions (ORR) are clarified by the dissociation and the change in Gibbs free energies for the elementary reaction steps of O₂ on Pd_{ML}/NbC(001).

1. Introduction

The oxygen reduction reaction (ORR) is a crucial step to the electrochemical energy conversion in the proton exchange membrane fuel cells (PEMFCs) [1–3], and the activity of catalysts for promoting adsorption and dissociation of O₂ may preliminary reflect the catalytic properties for ORR [4–6].

Considering the market requirements of PEMFCs, there are four standards to select the catalysts: corrosion resistance, low cost, high stability and high catalytic activities [7–9]. The traditional catalysts for PEMFCs are Pt-based catalysts with Pt loading on the carbon supports (denoted as Pt/C), which have many problems, e.g. the poor corrosion

resistance of the carbon substrate, the low durability of the Pt/C composite architecture, the dissolution of the catalyst, as well as the unexpected poisoning of Pt by the generated O or OH [10–12]. Besides, the high cost and scarcity of Pt hinder the large-scale application of Pt/C [13–15]. Since the landmark paper which demonstrated the Pt-like properties of tungsten carbide by Boudart et al. [16], the transition metal carbides (TMCs) have attracted many interests in catalysis and surface science, due to their high melting temperature, extreme hardness and high thermal conductivity [17–19]. Moreover, the reduction of precious metal loading by using TMCs as supports offers a great opportunity for cost reduction in electrocatalytic applications. Recently, a method of loading the noble metals monolayer (ML) on TMCs supports

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(denoted as $M_{ML}/TMCs$) has been proposed [20–23], including the theoretical studies about loading Pt ML on TiC(001) [20], Pd ML on Mo_2C and WC [22] and Pd ML on TiC [23], as well as the experimental researches about Pt, Pd and Ag ML on NbC [21]. These $M_{ML}/TMCs$ exhibited exceeding activities and outstanding performances relative to the conventional Pt/C catalysts.

Among the transition metal carbides, NbC has easier synthesization conditions, e.g., lower synthesization temperatures and processing costs to form high surface area catalyst than WC and TiC. Besides, NbC is stable under condition of acid and alkali at hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) potential [21,24]. These advantages make NbC a superiorly alternative support. Indeed, the Pt, Pd and Ag MLs on NbC(111) have demonstrated Pt-like characteristics [21,25].

In the present work, we choose the flat NbC(100) as the substrate, which is a non-polarized surface with equal numbers of carbon and metal atoms and has been proved both theoretically and experimentally to be the most stable cleavage surface of NbC [12,25] among the low index surfaces. We compare the stability and activity of metals monolayers on NbC(001) to select the best catalyst according to the criteria for the ideal catalysts discussed above, i.e., corrosion resistance, high stability, low cost and high catalytic activities. In addition, Misbah et al. [26] proved that the high wetting ability between adsorbed metal and support is also important to catalysts. The properties of group 9–11 metals ($M = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au$) MLs on the NbC(001) surface, denoted as $M_{ML}/NbC(001)$, are systematically studied and compared with those of Pt. The essential qualities about the electrocatalysts (stability, wetting ability, corrosion resistance and catalytic activity) of all the complexes are used to select the best one to fit ORR. As known, the surface carbon atoms of TMCs are easily to be oxidized under high temperature by air, which may cause collapse and performance decay of the layered structures of the catalysts. While studies [23,27,28] have indicated that loading a metal layer as a skin on the substrate would protect it from corrosion, we speculate that the ideal adsorption sites of metal atoms for effective surface protection from corrosion would be the top of carbon sites (C-top). Firstly we estimate the stability and the wetting ability of the supported systems, $M_{ML}/NbC(001)$. Then the metal MLs stably binding on the C-top sites on the NbC(001) surface are picked out, which are considered to have strong ability of corrosion resistance. Next, we study the catalytic activities of the variety complex and select the best catalyst according to the performance discussed above. To convincingly prove the catalytic activities, the adsorption performances and dissociation path of O_2 together with the Gibbs free energies for the elementary reaction steps on the selected catalyst are tested.

2. Models and computation method

2.1. Models

The bulk NbC has a cubic NaCl structure, in which each anion is surrounded by six cations, and vice-versa. The calculated lattice parameter of the optimized bulk NbC is 4.48 Å, which is in good agreement to the previous experimental [29] and theoretical data [30]. The NbC(001) surface is modeled by 4-layer slabs (which has been used in previous study [24]) with a (2×2) (001) surface and separated by a vacuum layer of 15 Å along the z-direction to ensure the interactions between the slabs to be negligible. The NbC(001) surface is selected as the support of the metals MLs. While allowing the two outmost layers to relax freely in the process of geometry optimization, the other two lower layers in the slab are fixed. The optimized NbC(001) is displayed in Fig. 1(a) and the two-dimensional (2D) metals ML supported on the NbC(001) is considered and shown in Fig. 1 (b). The single metal atom is simulated using a large cell with the dimensions of $10 \times 10 \times 10$ Å and the Pt(111) is modeled using a supercell including a 4-layer slab with a (2×2) surface and a 15 Å vacuum layer. The growth manner of

a metal overlayer (taking the Pd overlayer as an example) on the NbC(001) surface by adding metal atoms one by one is displayed in the supporting information (SI).

2.2. Computational method

The spin-polarized density functional theory (DFT) calculations are performed using the Cambridge sequential total energy package (CASTEP) with ultrasoft pseudopotentials. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) approach [31] is used to describe the exchange correlation interaction. The 2s2p states of C, 3d4s states of Co, Ni, Cu, 4d5s states of Nb, Rh, Pd, Ag and the 5d6s of Ir, Pt, Au are regarded as valence electrons. The Brillouin zone integrations are performed using the Monkhorst-Pack (MP) [32,33] scheme for the k-point sampling, with a MP grid of $9 \times 9 \times 9$ for the bulk geometry optimization and single Gamma point for the energy calculations of metal atoms, and MP grids of $5 \times 5 \times 1$ and $21 \times 21 \times 1$ for the geometric optimizations and electronic analysis, respectively, for the surface systems. A plane-wave cutoff of 400 eV is selected for the expansion of Kohn-Sham orbital. Both of the selections of k-points and cutoff value are tested carefully to ensure convergence of the energy difference and other properties. For geometry optimization, the self-consistent field tolerance of electronic states is set to 10^{-5} eV/atom. The force on each atom is set to 0.03 eV/Å, with the max displacement converged to 0.001 Å, respectively.

According to the definition from Xia et al. [26], when adding the metal overlayers on NbC(001) surface, the tendency of metals wetting, i.e. whether the metals deposit as a film on the support or detach to form large particles on the support surface, has been assessed by the binding energy increment (dE_b) of the overlayer as compared with the cohesive energy of bulk metal.

The binding energy of the metal overlayer on NbC is defined as

$$E_b = E_{ML/NbC} - E_{NbC} - nE_M \quad (1)$$

The cohesive energy of bulk metal is defined as

$$E_{bulk,M}^{coh} = E_{M,bulk} - E_M \quad (2)$$

Therefore,

$$dE_b = E_b - nE_{bulk,M}^{coh} = E_{ML/NbC} - E_{NbC} - nE_{M,bulk} \quad (3)$$

Here, in the above equations, $E_{ML/NbC}$ and E_{NbC} are the total energies of the NbC substrate with and without metal overlayer, respectively. E_M and $E_{M,bulk}$ are the energies of a free metal atom and a bulk metal atom obtained from an independent bulk calculation, respectively.

The surface energy ($E_{M,surf}$) of a metal layer on NbC(001) is defined as that given by Sheng et al. [34].

$$E_{M,surf} = 1/n(E_{ML/NbC} - E_{NbC} - nE_{M,bulk}) \quad (4)$$

Actually, equations (3) and (4) are equivalent, except that $E_{M,surf}$ defined in (4) is the average value per metal atom of dE_b defined in (3). Therefore, we only choose the binding energy increment (dE_b) for further discussion.

For an O_2 molecule, the adsorption energy (E_{ads}) is calculated by,

$$E_{ads} = E_{O_2/substrate} - (E_{O_2} + E_{substrate}), \quad (5)$$

where $E_{O_2/substrate}$ and $E_{substrate}$ are the total energies of surfaces with and without the adsorbed O_2 molecule, respectively, and E_{O_2} is the energy of an isolated O_2 molecule.

3. Results and discussion

3.1. The stability and wetting tendency of $M_{ML}/NbC(001)$

Firstly, we investigate the metal overlayer ($M = Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au$) deposition on the NbC (001) surface. The absolute

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