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Cathode catalysts for fuel cell development: A theoretical study based on band structure calculations for tungsten nitride and cobalt tungsten nitrides

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ABSTRACT

Band structure calculations were performed for tungsten nitride, cobalt tungsten nitrides, and platinum slabs. The major requirements for the development of a superior cathode catalyst are: (1) that the Fermi level of the cathode catalyst is close to the energy level of the lowest unoccupied molecular orbital of O_2, the lowest unoccupied atomic orbital of an oxygen atom, and the lowest unoccupied atomic orbital of a hydrogen atom so that they can readily interact with one another; and (2) that the cathode catalysts have smaller ΔE value which represent the difference between the Fermi level and the peak position of the density of states of the O_p orbital of O_2 adsorbed on the catalyst. The active site structures of cobalt tungsten nitrides for activation of the oxygen reduction reaction were found to have the surface structure of Co–O–Co, which lowered the unoccupied orbital of the oxygen atom to approximately that of the Fermi level. However, this structure concomitantly lowered the Fermi level, which resulted in an increase in ΔE. Consequently, the optimal cathode catalyst regarding the surface conformation contains a Co–O–Co structure that is dispersed on the surface of the cobalt tungsten nitride. The cobalt tungsten oxynitride exhibited a catalytic activity for the oxygen reduction reaction. A linear dependence is observed between the ΔE and the oxygen reduction reaction offset potentials of the tungsten nitride, cobalt tungsten nitride, cobalt tungsten oxynitride, and platinum.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) represent a promising technology for solving the problems of energy shortage and global warming, because devices that run on these cells use cleaner energy conversion than those that run on fossil fuels. PEFCs can also be used in automobiles and home generators with the advantages of lower energy consumption and no CO_2 emission due to their low operating temperatures and compact sizes. Although platinum (Pt)-containing catalysts are available as electrode catalysts for PEFCs, they are very expensive. Alternatives to Pt catalysts are being developed through ongoing experimental and theoretical studies.

In previous studies, we have applied the transition metal carbides, such as bimetallic tungsten carbides [1,2] and molybdenum carbides [3,4], as anode catalysts with high activities. These transition metal carbide catalysts were not suitable as cathode catalysts. On the other hand, we have studied transition metal nitrides catalysts for hydrogenation, hydrodesulfurization and hydrodenitrogenation [5–7]. The transition metal nitrides are chemically inert in acidic solution which is one of the important factors of a cathode catalyst. Based on these results, the transition metal nitrides have been studied as cathode catalysts. Zhong et al. [8] reported that W_2N/C exhibited the maximum power density of 39.2 mW cm^{-2}. Choi and Kumta [9] investigated the synthesis, structure, and electrochemical properties of the tantalum and tungsten nitrides, and reported that the highest capacitance was 30 F/g for WN when tested at the scanning rate of 2 mV/s. Ota and co-workers [10] studied the oxygen reduction reaction (ORR) activity of TaO_xN_y having a chemical stability in acidic solution. We experimentally studied some transition metal nitrides as cathode catalysts and found that a tungsten nitride is better than the other transition metal nitrides and the addition of cobalt improves the ORR activity. Therefore, the tungsten and cobalt tungsten nitrides are theoretically studied in this paper.

In recent years, with dramatic improvements in the performance of low-cost computers, several theoretical studies of the catalytic properties of cathode catalysts for PEFCs have been undertaken. Regarding the band structure, Eberhart and MacLaren [11] studied the similarity of the band structures of the transition metal monocarbides and the late transition metals. They concluded that this similarity was responsible for the observed similarity in the catalytic properties between them. Nørskov and co-workers [12] introduced the d-band model, and used the density of states (DOS) to represent the band structure in order to rationalize the activities of the noble metals and transition metal carbides [13,14]. The

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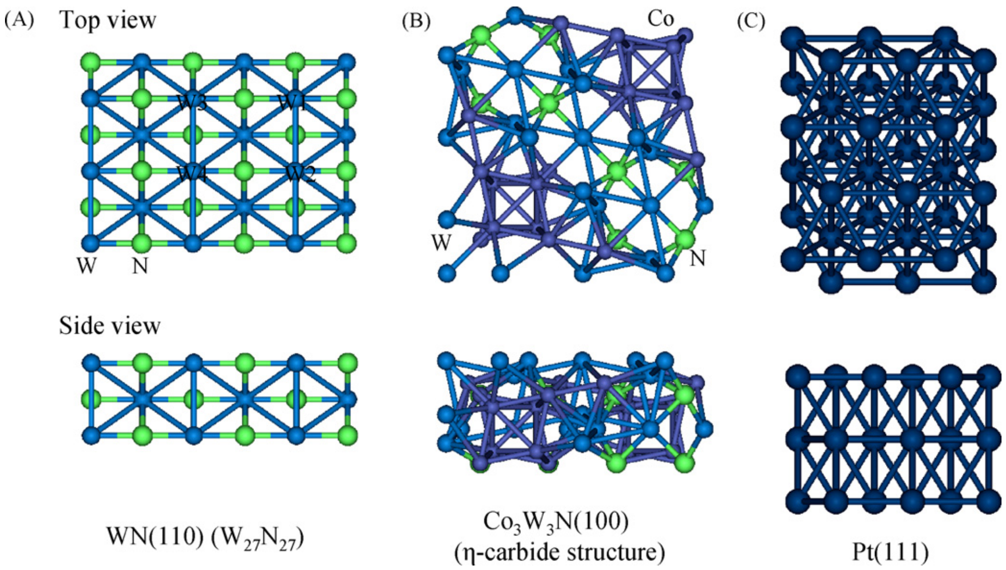

Fig. 1. Top and side views of the (A) WN(1 1 0), (B) Co_3W_3N, and (C) Pt(1 1 1) slabs used in the calculations.

d-band center is calculated as the first moment of the projected d-band DOS on the surface atoms with reference to the Fermi level. Kitchin et al. [13] described the relationship between the d-band center and the dissociative adsorption energies of H_2 and O_2 on Pt(1 1 1) slabs that contained below the surface other 3d metals. These relationships have important implications for the anode and cathode catalysts. Stamenkovic et al. [15] studied the d-band center to estimate of the ORR activities on the Pt_3M (M = Ni, Co, Fe, and Ti), and revealed the volcano-shaped dependence between the ORR activity and the d-band center. Adzic and co-workers [16,17] also reported the correlation between the d-band center and the ORR activities on the surfaces of Au(1 1 1), Ag(1 1 1), Pd(1 1 1), Rh(1 1 1), Ir(1 1 1), and Ru(0 0 0 1) on Pt monolayers, revealing a volcano-type dependence. The value of the d-band center is calculated relative to the Fermi level, and consequently, the Fermi level value is directly hidden. This quantification is an advantage when using the d-band center, however, we consider that the value of the Fermi level is an important factor for the cathode activity. Therefore, we paid attention to the DOS of oxygen rather than the metal d-band. In the present study, the band structures of the tungsten nitrides and cobalt tungsten nitrides both before and after the adsorption of O_2 were calculated, to examine the relationship between the band structure and catalytic activity as a cathode. For adoption as a cathode catalyst, two of the requirements had to be met. The band structure of platinum is discussed for comparative purposes.

2. Theoretical method

Self-consistent, gradient-corrected, periodic DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [18–21]. The calculations were performed using the projector-augmented wave (PAW) method [22,23] with generalized gradient (GGA) corrections as proposed by Perdew et al. [24]. For the plane wave set, a cutoff energy of 680 eV was used. The convergence criteria for the energy calculation and structure optimization were set to the SCF tolerance level of 1.0×10^{-6} eV and maximum force tolerance of 0.02 eV/Å. For calculations of the band structure, the geometry was initially optimized by restricting the Brillouin zone of the Γ point, and thereafter, the calculation was performed by a 15 k-point sampling through the series: $\Gamma(0\,0\,0) \rightarrow X(0.5\,0\,0) \rightarrow M(0.5\,0.5\,0) \rightarrow \Gamma(0\,0\,0)$. The supercell (10.00 Å × 10.00 Å × 10.00 Å) was used for the calculation of the molecular and atomic orbitals of O_2, O, and H. The structures of the WN(1 1 0), Co_3W_3N(1 0 0), and Pt(1 1 1) slabs used in the calculations are shown in Fig. 1. The periodically repeated orthorhombic supercells used for the WN(1 1 0), Co_3W_3N(1 0 0), and Pt(1 1 1) slabs were (12.36 Å × 8.76 Å × 20.00 Å), (11.10 Å × 11.10 Å × 20.00 Å), and (8.32 Å × 9.64 Å × 20.00 Å), respectively. For WN(1 1 0), a three-layer slab was used that contained 27 W atoms and 27 N atoms (Fig. 1A). For the cobalt tungsten nitride models, a Co_3W_3N(1 0 0) slab with the η-carbide structure (Fig. 1B), as well as $Co_xW_{27-x}N_{27}$ (x = 2 or x = 4) slabs, which were based on the WN(1 1 0) slab structure, were used. The configurations of the $Co_xW_{27-x}N_{27}$ (x = 2 or x = 4) slabs were as follows. The $Co_2W_{25}N_{27}$a slab was modified by replacement of the W1 and W2 atoms (shown in Fig. 1A) by Co atoms. Similarly, the $Co_2W_{25}N_{27}$b slab was modified by replacement of the W1 and W4 atoms (Fig. 1A) by Co atoms. The $Co_4W_{23}N_{27}$ slab was modified by replacement of the W1–W4 atoms (Fig. 1A) by Co atoms. For the Pt(1 1 1) slab, the three-layer slab contained 36 Pt atoms (Fig. 1C). For the WN, the lattice constants were calculated as $a = b = c = 4.147$ Å, which was in good agreement with the JCPDS reference card 75-1012 [25] ($a = b = c = 4.13$ Å), with the relative error of 0.412%, i.e., error within 1%. Choi and Kumta [9] determined the lattice constants of WN by Rietveld refinement as $a = 4.12$ Å, which was also in good agreement with our calculated value. The lattice constant of Pt was calculated as $a = b = c = 3.978$ Å,

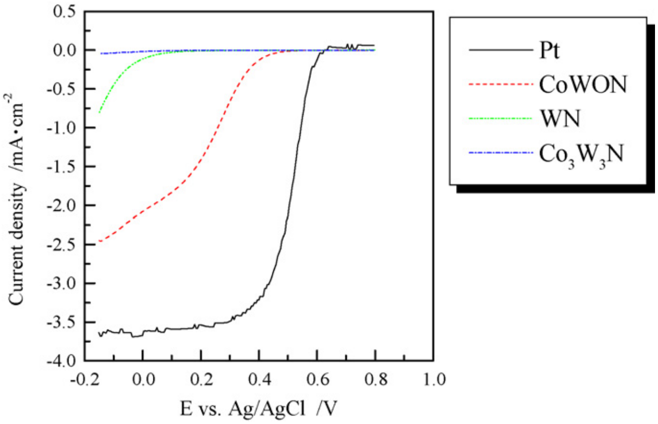

Fig. 2. The polarization curves of WN, Co_3W_3N, CoWON, and Pt.