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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Introduction

Although platinum-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 recent years, with dramatic improvements in the performance of low-cost computers, several theoretical studies of the catalytic properties of electrode catalysts for PEFCs are have been undertaken. Lima et al. [1] have reported a correlation between the d-band center and the activities of the oxygen reduction reaction (ORR) on the surfaces of Au(111), Ag(111), Pd(111), Rh(111), Ir(111), and Ru(0001) on Pt monolayers, revealing a volcano-type dependence. The value of the d-band center is calculated relative to the Fermi level, and the value of the Fermi level is directly hidden. This quantification primarily reflects the d-band center, although we consider that the Fermi level is also an important factor in the activity of a cathode catalyst. Therefore, we have focused on the band structure rather than the DOS. Eberhart and MacLaren [2] have shown that band structures are related to the catalytic activities of carbides, whereas band structures are not relevant to the performances of catalysts as electrodes. In the present study, the band structures of tungsten nitrides and cobalt tungsten nitrides both before and after the adsorption of O_2 were calculated, to examine the relationship between 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.

Theoretical Method

Self-consistent, gradient-corrected, periodic DFT calculations were performed using the VASP. The calculations were performed using the PAW method [3,4] with generalized gradient (GGA) corrections as proposed by Perdew et al. [5]. 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 the calculations of band structure, the geometry was initially optimized by restricting the Brillouin zone of the Γ point, and thereafter, the calculation was performed by 15 k-point sampling through the series: Γ(0,0,0)→X(0.5,0,0)→M(0.5,0.5,0)→Γ(0,0,0). The periodically repeated orthorhombic supercells used for the WN(110), Co_3W_3N(100), and Pt(111) 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(110), a three-layer slab was used that contained 27 W atoms and 27 N atoms. For the cobalt tungsten nitride models, a Co_3W_3N(100) slab with the η-carbide structure, as well as $Co_xW_{27-x}N_{27}$ (x=2 or x=4) slabs. 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 to Co atoms. Similarly, the $Co_2W_{25}N_{27}$b slab was modified by replacement of the W1 and W4 atoms to Co atoms. The $Co_4W_{23}N_{27}$ slab was modified by replacement of the W1-W4 atoms to Co atoms. This section serves as the "Experimental" section for laboratory studies. Brief descriptions of chemicals and equipment should be supplied, along with descriptions of experimental procedures, analytical tools and methods of data analysis. For studies, which are exclusively theoretical or computational, descriptions of relevant software packages, basis sets, data analysis tools, etc should be supplied.

Results and Discussion

The band structures of tungsten nitrides and cobalt tungsten nitrides before and after O_2 adsorption were calculated to reveal the relationship between band structure and catalytic activity as a cathode. Two essential requirements for an optimal valuable cathode catalyst are proposed: (1) that the Fermi level of the cathode catalyst is sufficiently close to the energy levels of $O_{2\,LUMO}$ and O_{LUAO} so as to interact readily; and (2) the cathode catalyst should have a small energy difference (ΔE), defined as the difference between the Fermi level and the peak position of the O_p DOS of the absorbed O_2 on the catalyst. The active surface structures of the cobalt tungsten nitrides consisted of Co-O-Co, as this structure lowered the unoccupied orbital of O close to the Fermi level. However, this Co-O-Co structure concomitantly lowered the Fermi level, resulting in a larger value for ΔE. Consequently, the most desirable cathode catalyst has a surface conformation of Co-O-Co structures that are moderately dispersed on the surface of the cobalt tungsten nitride. Furthermore, when the cobalt tungsten oxynitride is not oxidized at the site neighboring the cobalt atom there results a much superior cathode catalyst.

References

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	E_f (Clean slab) [eV]	E_f (After O_2 adsorption) [eV]	Energy level [eV]	O_p DOS peak (E_p) [eV]	ΔE[a] [eV]
WN(110)	-1.117	-1.095	-	0.017	1.112
$Co_2W_{25}N_{27}$a	-1.069	-1.197	-	-0.869	0.328
$Co_2W_{25}N_{27}$b	-1.075	-1.091	-	0.104	1.195
$Co_4W_{23}N_{27}$	-1.147	-1.443	-	-0.827	0.616
Co_3W_3N(100)	-1.816	-1.990	-	-0.413	1.577
Pt(111)	-1.220	-1.167	-	-1.126	0.041
O_2 LUMO	-	-	-0.232	-	-
O LUAO	-	-	-0.311	-	-

[a] $\Delta E=E_p-E_f$(after O_2 adsorption).