

Ab initio analysis of sulfur tolerance of Ni, Cu, and Ni–Cu alloys for solid oxide fuel cells

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Abstract

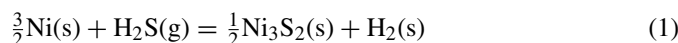
Interactions between sulfur and Ni_{1-x}Cu_x ($x = 0.00, 0.25, 0.50, 0.75, \text{ and } 1.00$) were examined by a first-principles analysis based on density functional theory (DFT) calculations to provide a scientific basis for intelligent design of sulfur-tolerant anode materials for solid oxide fuel cells (SOFCs). Examination of slab models with three and five atomic layers for Ni and Cu (1 1 1) surfaces indicates that sulfur species may adsorb on four types of sites: atop, bridge, hcp hollow, and fcc hollow, among which the fcc-hollow centers are the most energetically favorable. The adsorption energy of sulfur on Ni is approximately 20% higher than that on Cu for both unrelaxed and relaxed five-layer surface models, which is qualitatively in good agreement with experimental observations. Using two active sites at three-fold hollow sites, the adsorption energy for sulfur on Ni_{1-x}Cu_x is predicted as a function of the alloy composition. Alloying Ni with Cu improves sulfur tolerance, however not to the degree of pure Cu.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention because of their high energy efficiency and fuel flexibility [1]. SOFCs can use not only hydrogen but also hydrocarbon fuels, bio-fuels, and gasified coal [2–4]. While direct utilization of hydrocarbon fuels in SOFCs are possible [5,6], various intrinsic problems associated with hydrocarbon fuels have to be resolved, including coking and sulfur-poisoning of anode materials. Cu-based anode materials have been extensively studied since Cu exhibits better tolerance to carbon deposition and sulfur than Ni-based anodes [2,3]. In principle, sulfur-poisoning is originated from either formation of atomic sulfur on the anode surface via decomposition of hydrogen sulfide (H₂S) or formation of nickel sulfide according to Eq. (1) [7].



Recently nickel sulfides formed on the surface of Ni–yttria-stabilized zirconia (YSZ; 8 mol.% Y₂O₃) cermet and NiO–YSZ

composite have been identified using Raman spectroscopy after exposure to H₂ fuel containing 100 ppm H₂S at 1000 K for 5 days [8]. Although various experimental and theoretical calculations have been performed [2,3,9–15], to the best of our knowledge, a direct comparison of sulfur tolerance on Ni and Cu surfaces at the same level of periodic density functional theory (DFT) has not yet been reported in the literature. Understanding the adsorption of surface sulfur species at the molecular level is crucial to the development of new sulfur-tolerant anode materials for SOFCs. In this study, we report the stability of Ni- and Cu-based anode materials in sulfur-containing fuels as predicted by periodic and self-consistent DFT calculations based on the most densely packed fcc (1 1 1) surfaces. We have estimated vibrational frequencies and partial charges with various optimized structures of adsorbed sulfur on Ni(1 1 1) and Cu(1 1 1) surfaces. Furthermore, using two active sites at three-fold hollow sites, we have examined the sulfur tolerance as a function of the Ni and Cu alloy composition.

2. Computational methods

Electronic structure calculations of Ni–Cu clusters were carried out using the hybrid density functional B3LYP [16–18] method with the 6-311+G(d)

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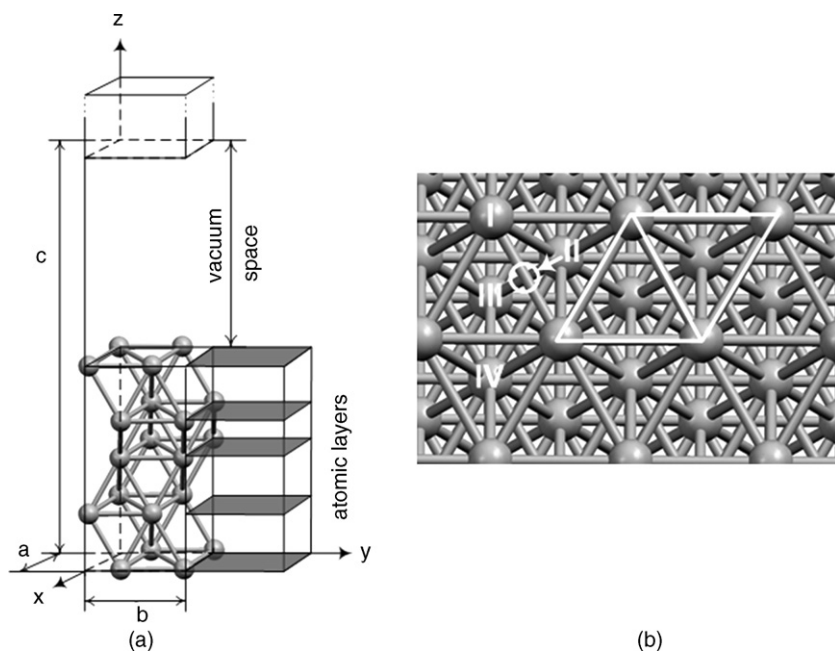


Fig. 1. (a) A schematic of a slab model and (b) four active sites for predicting the adsorption energies of sulfur species on $\text{Ni}_{1-x}\text{Cu}_x(1\ 1\ 1)$ surface: I, II, III and IV correspond to atop, bridge, hcp hollow, and fcc hollow. A rhombus represents a $p(2 \times 2)$ unit cell.

[19] basis set as implemented in the Gaussian 03 program package [20]. The slab model calculations were performed using the Vienna ab initio simulation package (VASP) code [21,22] mostly with the projector augmented wave method (PAW) [23,24]. The exchange and correlation energies were described by generalized gradient approximation (GGA) using the Perdew–Wang (PW91) functional. Brillouin-zone integrations were performed on grids of $(6 \times 6 \times 6)$, $(6 \times 6 \times 1)$ and $(3 \times 3 \times 1)$, and $(5 \times 5 \times 1)$ k-point meshes with the Monkhorst–Pack method [25] for bulk, three- and five-layer slab models, respectively. Cut-off energies of 300 and 400 eV were used for three- and five-layer slab models, respectively. The parameters of k-points and cut-off energies were allowed to converge to 0.01 eV in the total energy. In this study, all slabs were separated by a vacuum spacing greater than 10 Å (see Fig. 1(a)), which guarantees no interaction between slabs. Geometry optimizations were executed by the conjugate-gradient algorithm.

To investigate the sulfur tolerance, we initially calculated adsorption energies according to Eq. (2) on a three-layer super cell in which each layer has one metal atom.

$$\Delta E_{\text{ads}} = E[\text{substrate}] + E[\text{S}] - E[\text{substrate} + \text{S}] \quad (2)$$

where, $E[\text{substrate}]$, $E[\text{S}]$, $E[\text{substrate} + \text{adsorbent}]$ are the calculated energies of bare metal surface, sulfur atom, and adsorbed sulfur species on the metal surface, respectively. Thus, more positive adsorption energy corresponds to more stable adsorption or less sulfur-tolerant. The spin-polarized method [26] was applied for an isolated sulfur atom. According to Kresse and Hafner [27] and Mittemdorfer and Hafner [28], the magnetic effect for $\text{Ni}(1\ 1\ 1)$ by spin-polarization calculations is insignificant for adsorption energies and geometries. Thus, all calculations were carried out with non-spin-polarization methods. More detailed adsorption-energy calculations were done on a five-layer super cell [29,30] in which each layer has four atoms to represent a $p(2 \times 2)$ unit cell that corresponds to a surface coverage of 0.25 monolayer (ML). As illustrated in Fig. 1(b), four active sites were examined, including “atop,” “bridge,” “hcp hollow,” and “fcc hollow,” referring to adsorption of sulfur atom to one, two, and three metal atoms, respectively. Note that the center atoms for hcp- and fcc-hollow sites are located on the second and third layers, respectively. Moreover, vibrational frequencies were calculated, providing a scientific basis for investigations into sulfur-tolerant anode materials using vibrational spectroscopy. Partial charges of adsorbed sulfur species were calculated using the Bader program, which provides more accurate atomic charges than Mulliken analysis for plane wave basis functions [31,32].

3. Results and discussion

3.1. Cluster-model calculation and bulk structures

Cluster-model calculations for the sulfur tolerance on Ni and Cu metals were carried out at the B3LYP/6-311+G(d) level of theory [20]. Table 1 lists the optimized parameters and adsorption energies for interactions of a sulfur atom with monometallic Ni and Cu and bimetallic NiCu-based clusters. The ground-state multiplicity varies from singlet to triplet. Predicted adsorption energies of both monometallic and bimetallic clusters are qualitatively in good agreement with the available experimental data; Cu is more sulfur-tolerant than Ni [2,3]. In order to more realistically model the sulfur tolerance using slab models [33], we first optimized bulk structures to determine the equilibrium lattice constants of $\text{Ni}_{1-x}\text{Cu}_x$ ($x=0.00, 0.25, 0.50, 0.75$, and 1.00). The estimated bulk lattice constants for pure $\text{Ni}(1\ 1\ 1)$ and $\text{Cu}(1\ 1\ 1)$ are 3.53 and 3.64 Å, respectively, which are in good agreement with experimental values of 3.52 and 3.61 Å [34], respectively. For bimetallic $\text{Ni}_{1-x}\text{Cu}_x$ ($x=0.25, 0.50$, and 0.75), calculated bulk lattice constants are 3.66, 3.65, 3.64 Å, respectively.

Table 1
Predicted adsorption energies and bond lengths for atomic sulfur interaction with atomic and bimetallic clusters

	Ni–S	Cu–S	Ni–S–Ni	Ni–S–Cu	Cu–S–Cu
Multiplicity ^a	3	2	3	2	1
d^b (Å)	1.986	2.072	2.131	2.123	2.132
Adsorption energy (kJ mol ⁻¹)	402.1	142.5	370.5	354.2	320.1

^a Multiplicity for ground state.

^b The distance between metal or surface and sulfur atom.

Table 2
Estimated parameters for atomic sulfur interactions on Ni(1 1 1) and Cu(1 1 1) with three-layer p(1 × 1) surfaces

	Ni(1 1 1)		Cu(1 1 1)	
Surface area (Å ²)	6.17		6.56	
Bond length ^a (Å)	2.483	2.492 ^a	2.574	2.556 ^a
Work function (eV)	5.23	5.15 ^b	4.80	4.65 ^c
Work function (kJ mol ⁻¹)	504.6	496.9 ^b	463.1	448.6 ^c
<i>d</i> ^d (Å)	2.148		2.300	
Adsorption energy (kJ mol ⁻¹)	290.6		262.9	
<i>v</i> (cm ⁻¹)	262		205	

^a The distance between metals.

^b From Ref. [35].

^c Experimental data from <http://environmentalchemistry.com/yogi/periodic/>.

^d The distance between metal and sulfur atom.

3.2. Ni(1 1 1) and Cu(1 1 1)

Three- and five-layer surface models were applied for slab model calculations.

3.2.1. Sulfur tolerance of Ni and Cu on three-layer surface model

The bulk Ni and Cu were optimized on a three-layer super cell that has a p(1 × 1) unit cell that corresponds to a surface coverage of one monolayer. As shown in Table 2, the predicted bond distances of Ni–Ni and Cu–Cu are in line with experimental data [35]. For the surface calculations on the sulfur tolerance, the atoms in the two topmost layers and adsorbed species were allowed to relax. We found a slight surface reconstruction by the atomic sulfur adsorption. Table 2 summarizes estimated adsorption energies, geometrical parameters, and vibrational frequencies on three-layer Ni and Cu surfaces. Similar to the cluster-model calculations, Cu is more sulfur-tolerant than Ni in terms of adsorption energy, which agrees with experimental observation [2,3]. However, the bond distance between Ni and adsorbed sulfur species is inconsistent with the surface–sulfur distances (1.40 Å [9], 1.50 Å [14], 1.68 Å [11], and 1.70 Å [13]) measured by various experimental techniques. Our predicted

vibrational frequency for Ni–S stretching mode is shifted from the predicted results by Yang and Whitten [15], 355–460 cm⁻¹.

3.2.2. Sulfur tolerance of Ni_{1-x}Cu_x(1 1 1) on five-layer surface model

In order to obtain more reasonable theoretical results, we applied a five-layer p(2 × 2) slab model as depicted in Fig. 2. Table 3 compiles calculated adsorption energies, geometrical parameters, and vibrational frequencies on unrelaxed and relaxed Ni_{1-x}Cu_x(1 1 1) (*x*=0.00 and 1.00) surfaces. We found a slight surface reconstruction by the atomic sulfur adsorption. However, surface sulfur reconstruction effects are minor in the energetics (<8.0 kJ mol⁻¹ ≈83 meV) and geometrical parameters (<0.03 Å). Fig. 3 shows that the adsorption energies on the unreconstructed Ni and Cu surfaces increase from 364.8 to 521.3 kJ mol⁻¹ and from 300.3 to 415.8 kJ mol⁻¹, respectively, while those on the relaxed surfaces increase from 377.9 to 524.6 kJ mol⁻¹ and from 310.6 to 420.8 kJ mol⁻¹, respectively. It has been experimentally proven [9,11,13,14] that the three-fold hollow site is the most favorable for sulfur adsorption on Ni surfaces by different techniques, in which the surface–sulfur distance varies to 1.40 Å [9], 1.50 Å [14], 1.68 Å [11], and 1.70 Å [13]. Our estimated distance of 1.547 Å on the fcc site is consistent with these experimental observations. The adsorption energies on the Cu surface estimated in this study are also in good agreement with previous predictions both by slab [10] and cluster [12] models. Weaker sulfur binding is exhibited by adsorption on Cu(1 1 1) than Ni(1 1 1). The fcc-hollow sites with adsorption energies of 415.8 and 420.8 kJ mol⁻¹ represented in Table 3 and Fig. 3 are the most stable, similar to those on the Ni(1 1 1) surface.

The average value of the calculated surface–sulfur stretching vibrational frequency on the Ni surface in Table 1 is 447 cm⁻¹, which is consistent with the predicted results by Yang and Whitten [15], 355–460 cm⁻¹, within the uncertainty of the computational method used. Smaller vibrational frequencies on Cu(1 1 1) are attributable to weaker binding energies. The predicted vibrational frequencies provide a scientific basis for the interpretation

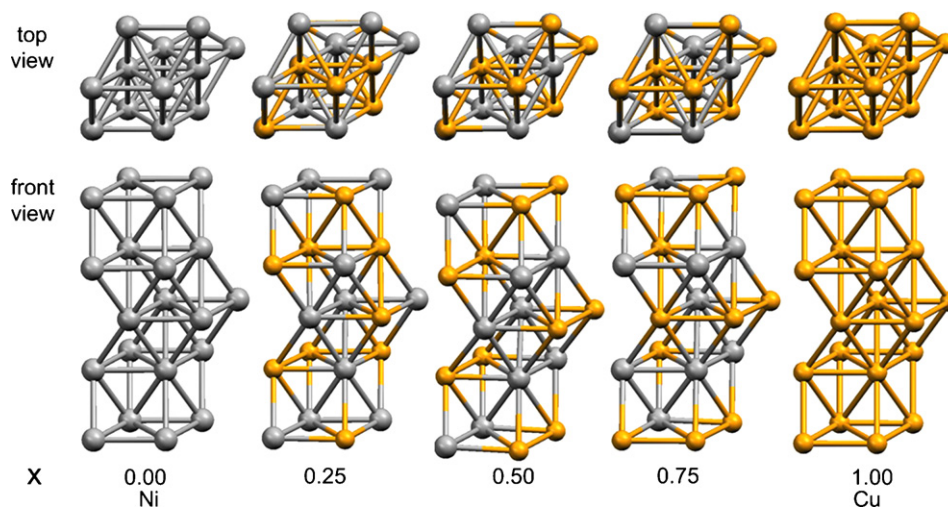


Fig. 2. Supercell models of homogeneous Ni_{1-x}Cu_x as a function of the alloy composition. Ni and Cu are in gray and in brown, respectively.

Table 3
Predicted adsorption energies, bond lengths, vibrational frequencies for atomic sulfur interaction on five-layer Ni(1 1 1) and Cu(1 1 1) surfaces

Active site	Ni(1 1 1) ^a				Cu(1 1 1) ^a			
	1 atop	2 bridge	3		1 atop	2 bridge	3	
			hcp hollow	fcc hollow			hcp hollow	fcc hollow
Unrelaxed								
Adsorption energy (kJ mol ⁻¹)	364.8	488.0	519.1	521.3	300.3	391.8	413.7	415.8
<i>h</i> ^b (Å)	1.976	1.664	1.588	1.592	2.049	1.746	1.664	1.659
<i>d</i> ^c (Å)	1.976	2.066	2.128	2.131	2.049	2.159	2.218	2.215
<i>v</i> (cm ⁻¹)	514	437	433	429	396	384	374	384
Relaxed								
Adsorption energy (kJ mol ⁻¹)	377.9	502.3	523.1	524.6	310.6	406.2	417.0	420.8
<i>h</i> ^b (Å)	2.002	1.619	1.554	1.547	2.083	1.687	1.628	1.619
<i>d</i> ^c (Å)	2.002	2.082	2.122	2.118	2.083	2.170	2.218	2.215
<i>v</i> (cm ⁻¹)	495	447	439	441	416	418	408	387

^a 1, 2, and 3 are coordination numbers.

^b Vertical distance between surface and sulfur atom.

^c The shortest distance between metal and adsorbed sulfur atom.

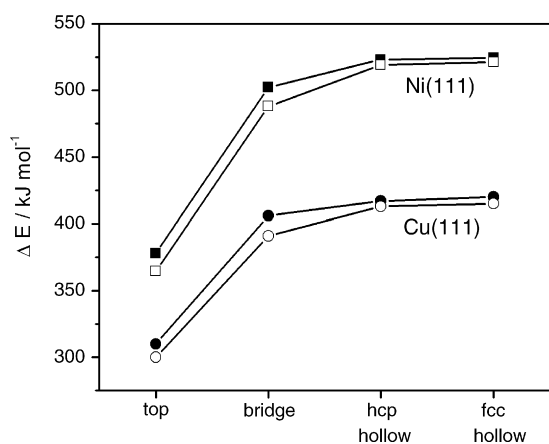


Fig. 3. Comparison of the predicted adsorption energies of atomic sulfur on three-top layer relaxed Ni(1 1 1) (■) and Cu(1 1 1) (●) surfaces and on unrelaxed Ni(1 1 1) (□) and Cu(1 1 1) (○) surfaces at the four different active sites.

of adsorbed sulfur species on anode materials in SOFCs by means of vibrational spectroscopy [8].

Chemisorption leads to electron transfer between Ni and Cu surfaces and adsorbed sulfur species. As summarized in Table 4, partial charges of adsorbed sulfur species on unrelaxed and relaxed Ni(1 1 1) and Cu(1 1 1) surfaces were calculated using the Bader charge analysis [31,32]. Charge transfer from the metal surfaces to adsorbed sulfur species occurs, leaving the adsorbates negatively charged. The sulfur species on the relaxed

Table 4
Partial charges of adsorbed sulfur species on Ni(1 1 1) and Cu(1 1 1)

Atop		Bridge		hcp hollow		fcc hollow	
I	II	I	II	I	II	I	II
Ni(1 1 1) ^a							
-0.40	-0.43	-0.40	-0.44	-0.40	-0.41	-0.38	-0.40
Cu(1 1 1) ^a							
-0.41	-0.53	-0.47	-0.51	-0.46	-0.52	-0.49	-0.48

^a I and II correspond to calculations on unrelaxed and relaxed surfaces.

surfaces become more negatively charged than those on the unrelaxed surfaces for all active sites except the fcc-hollow site of Cu. Moreover, the charge transfer from Cu to the adsorbates is slightly higher than that from Ni.

Similar to pure Ni and Cu metal surfaces ($x=0.00$ and 1.00 , respectively), we examined the sulfur tolerance as a function of the Ni and Cu alloy composition, i.e., $x=0.25$, 0.50 , and 0.75 , using periodic slab models (see Fig. 2). The calculations were performed with the relaxed surfaces. Since the optimization processes at atop and bridge produced indistinguishable structures, the calculations were carried out using two active sites at three-fold hollow sites. As displayed in Fig. 4, sulfur adsorption energies follow Raoultian relation with Cu addition. Alloying Ni with Cu improves theoretical sulfur tolerance; however, bimetallic compositions have higher adsorption energies than pure Cu. In addition, changing the pseudopotentials from GGA-PAW to ultrasoft pseudopotentials has only minor effects on the adsorption-energy calculations. The step-wise mechanisms of H₂S decomposition on Ni- and Cu-based anode surfaces in an SOFC are predicted using detailed quantum-chemical calculations [36].

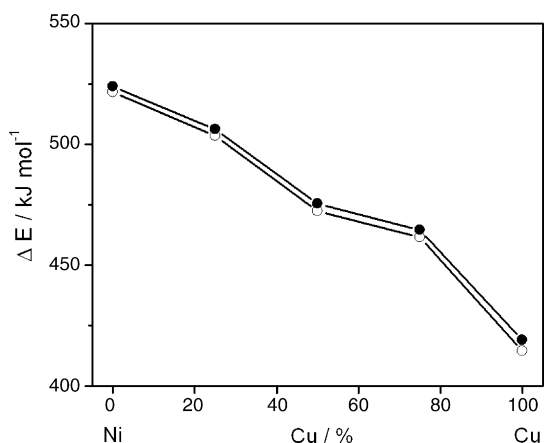


Fig. 4. Comparison of the predicted adsorption energies of atomic sulfur on Ni_{1-x}Cu_x(1 1 1) at PAW-GGA-DFT (●) and GGA-DFT (○).

4. Conclusion

Sulfur tolerance on the Ni and Cu metals and their alloys surfaces were investigated by means of DFT calculations. Based on the adsorption-energy comparison, Cu is more sulfur-tolerant than Ni at all four active sites, which is qualitatively in line with available experimental results, implying that the theoretical determination of stability can guide the design of new sulfur-tolerant anode materials in SOFCs. Alloying Ni with Cu improves sulfur tolerance, however not to the degree of pure Cu.

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