Near Neutrality of an Oxygen Molecule Adsorbed on a Pt(111) Surface

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The charge state of paramagnetic or nonmagnetic O₂ adsorbed on a Pt(111) surface is analyzed using density functional theory. We find no significant charge transfer between Pt and the two adsorbed molecular precursors, suggesting these oxygen reduction reaction (ORR) intermediates are nearly neutral, and changes in magnetic moment come from self adjustment of O₂ spin-orbital occupations. Our findings support a greatly simplified model of electrocatalyzed ORR, and also point to more subtle pictures of adsorbates or impurities interacting with crystal than literal integer charge transfers.

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The adsorption of an O₂ molecule on a metal surface is an important process in surface physics and electrocatalysis [1–5]. Although the atomic geometries of O₂ adsorption can be accurately measured [1–4], the charge state of O₂ (∗ means adsorbed state or a free adsorption site) can only be inferred by indirect means such as vibrational frequency measurement. Under ultrahigh vacuum conditions, two bands of stretching mode of O₂ on Pt (111) surface, 860–880 and 690–700 cm⁻¹, were identified and assigned as superoxide O₂⁻ and peroxide O₂²⁻ ion, respectively [1–3]. The charge assignment is crucial for understanding the mechanism of electrochemical oxygen reduction reaction (ORR), a complex multielectron transfer process. There has been a long debate on the existence of O₂⁻ as the intermediate in ORR [6]. Recently, Shao et al. measured oxygen vibrational spectra on Pt electrode in aqueous solution and suggested the formation of O₂⁻ as the first reaction step in electrocatalyzed ORR [5].

Ab initio modeling provides means to investigate the electronic structure of O₂⁻ quantitatively. Eichler and Hafner used density functional theory (DFT) calculation to study O₂ adsorption and identified superoxide O₂⁻ as a paramagnetic chemisorbed precursor at the bridge site of Pt(111) surface, and peroxide O₂²⁻ as a nonmagnetic precursor at the fcc hollow site, illustrated in Fig. 1(a) [7,8]. The formal charge assignments 1⁻ and 2⁻ were based on magnetic moments, vibrational frequencies and the shape of the charge difference density \( \Delta \rho \equiv \rho[Pt(111) + O_2] - \rho[Pt(111)] - \rho[O_2] \) for these two O₂⁻ precursors. Since the vertical distance between O₂⁻ and surface is about 2 Å [7,8], these charge assignments would indicate large induced dipoles, defined as the difference in supercell total dipole before and after O₂ adsorption. However, this contradicts Hyman and Medlin’s DFT study of oxygen molecule and atom adsorption on Pt(111) surface, where it was found that the induced electric dipole moments are very small (0.07 and 0.04 Åe for O₂⁻ and O⁺, respectively) [9].

There is an urgent need to resolve this contradiction in order to understand the charge-transfer sequence of electrochemical ORR [10–12]. Recently, Nørskov et al. proposed a model to explain the origin of the \( \sim 0.4 \) volt cathode overpotential for ORR on Pt, as well as rank alloy catalytic activities, in significant agreement with experiments [12]. In this model, all the adsorbates such as O₂⁺, OOH⁺, O⁺, and OH⁺ are assumed to be charge neutral, so the 4 electron transfers always occur concurrently with the 4 proton (hydronium) transfers from the electrolyte; i.e., all electron transfers are proton-coupled (PCET) [13].

Energy landscapes of the electrochemical ORR as a function of the electrode potential \( V \) were obtained, with the underlying assumption that the adsorption free energies of reaction intermediates are unaffected by \( V \). This means very small electric dipoles induced by O₂⁻, OOH⁺, O⁺, and OH⁺ in the surface normal direction, synonymous with the near-neutrality of these adsorbates, which needs to be justified in view of the conflicting reports [5,7–9].

To resolve this critical issue, we perform ab initio calculations of the adsorption of O₂ on Pt(111) surface and analyze the charge and spin densities quantitatively. We identify that there is no significant charge transfer between Pt surface and two chemisorbed precursors (paramagnetic and nonmagnetic). The change in magnetic moment is achieved by self-adjustments of occupations in two \( \pi^* \) antibonding orbitals in O₂⁻.

![FIG. 1 (color online). (a) Configurations of two chemisorbed O₂ molecular precursors at the bridge site and fcc hollow site. (b) Molecular orbital energy diagram for O₂.](image-url)
The calculations are performed using VASP [14,15]. We use projector augmented wave (PAW) potentials [16] with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [17] in spin-polarized condition. The Pt(111) surface is modeled by a four-layer slab with a rectangular $\sqrt{3} \times 2$ unit cell of total 16 Pt atoms, separated by 12 Å thick vacuum layer. Only one oxygen molecule is adsorbed on one side of the slab: the molecule and Pt atoms at the top two layers are fully relaxed. Brillouin zone integrations are performed on a grid of $4 \times 4 \times 1 \tilde{k}$ points, using first-order Methfessel-Paxton smearing of $\sigma = 0.2$ eV. The calculations are performed at equilibrium lattice constant of $a_0 = 3.977$ Å. Dipole corrections [18] of the electric potential and total energy are imposed to eliminate dipole-dipole interactions between image supercells. We have also checked the effects of larger supercell, symmetric adsorptions on both sides of the slab, larger vacuum region, higher density $\tilde{k}$-points sampling in Brillouin zone and the usage of ultrasoft pseudopotentials with different functionals (LSD, PW91). In all cases, the changes in $O_2^+$ charge state are not significant.

Table I shows the optimized geometry, $E_{\text{ad}}$, magnetic moment $m$, and stretching frequency $\nu$ of adsorbed $O_2^+$, most of which agree with Eichler and Hafner’s results by ultrasoft pseudopotentials [7,8] and Shao’s DFT calculations [5]. The magnetic moment density and total charge difference density are plotted and their shapes are seen to match Eichler and Hafner’s plots [7,8]: for $O_2^+$ at bridge site, its remaining magnetic moment density behaves like $\pi^+$ antibonding orbital; meanwhile, the shape of the charge difference density $\Delta \rho$ is similar to the $\pi_1^+$ antibonding orbital [the molecular orbital energies of free $O_2$ are illustrated in Fig. 1(b), || and \perp means parallel and perpendicular to the metal surface, respectively], so it was suggested that about one electron transferred from Pt to $\pi_1^+$ spin-down orbital. On the other hand, for $O_2^+$ at fcc hollow site, there is no magnetic moment left, and the shape of the charge difference density is like the sum of $\pi_1^+$ and $\pi_1^-$, so it was suggested that about two electrons transferred from Pt to both $\pi_1^+$ and $\pi_1^-$ spin-down orbitals. However, the induced dipole $P_z$, computed by direct charge integration in the supercell, is found by us to be small, only 0.06 and 0.07 eÅ for the bridge and fcc hollow site, respectively.

To analyze the charge state in a more fine-grained manner, we integrate the charge difference densities in the total charge, but there is a tremendous cancellation effect between $\Delta \rho_1$ and $\Delta \rho_f$. Using similar definition as Eqn. (1) for $\Delta N_f$, the spin-charge transfer for paramagnetic $O_2^+$ at bridge site is found to be $\Delta N_f = -0.64e$ and $\Delta N_i = 0.71e$. Meanwhile, the isosurfaces of $\Delta \rho_1$ and $\Delta \rho_f$ [Fig. 2(a)] indicate that most of the spin-charge changes result from the decreased occupation of $\pi_1^+$ spin-up orbital and increased occupation of $\pi_1^+$ spin-down orbital. Such $\pi_1^+ \rightarrow \pi_1^+$ transfer, illustrated in Fig. 1(b), causes no change in the total charge density, and thus would not be detectable in the total charge difference $\Delta \rho$ plot in spite of large activity.

For nonmagnetic $O_2^+$ at fcc site, $\Delta N_i = -0.93e$ and $\Delta N_f = 1.02e$. The isosurfaces of $\Delta \rho_1$ and $\Delta \rho_f$ [Fig. 2(b)] show that both spin-charge differences have similar shape, which is a combination of $\pi_1^+$ and $\pi_1^-$ orbitals, but are

**TABLE I.** DFT-PBE-PAW optimized $O_2^+$ molecular precursors on Pt(111): the equilibrium bond length $b$, vertical distance $z$ between $O_2^+$ center and surface, adsorption energy $E_{\text{ad}}$, magnetic moment $m$, stretching frequency $\nu$, and induced vertical electric dipole $P_z$.

<table>
<thead>
<tr>
<th></th>
<th>$b$ [Å]</th>
<th>$z$ [Å]</th>
<th>$E_{\text{ad}}$ [eV]</th>
<th>$m$ [$\mu_B$]</th>
<th>$\nu$ [cm$^{-1}$]</th>
<th>$\nu_{\text{exp}}$ [cm$^{-1}$]</th>
<th>$P_z$ [eÅ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>bridge</td>
<td>1.35</td>
<td>1.91</td>
<td>-0.65</td>
<td>0.93</td>
<td>913</td>
<td>870 [1], 875 [2]</td>
<td>0.06</td>
</tr>
<tr>
<td>fcc hollow</td>
<td>1.39</td>
<td>1.74</td>
<td>-0.53</td>
<td>0.00</td>
<td>826</td>
<td>710 [1], 700 [2]</td>
<td>0.07</td>
</tr>
</tbody>
</table>

For nonmagnetic $O_2^+$ at fcc site, $\Delta N_i = -0.93e$ and $\Delta N_f = 1.02e$. The isosurfaces of $\Delta \rho_1$ and $\Delta \rho_f$ [Fig. 2(b)] show that both spin-charge differences have similar shape, which is a combination of $\pi_1^+$ and $\pi_1^-$ orbitals, but are...
sorbed at fcc hollow site, both spin-up and spin-down character of the Bloch eigenfunctions are paramagnetic and almost neutral state; when O$_2$ is adsorbed at bridge site, beside oxygen. For fcc-site case (b), isosurface of $\psi_3$ $(n = 89, \epsilon = 0.35$ eV) behaves as spin-up/down $\pi_\perp^*$, while $\psi_2/\psi_4$ $(n = 90, \epsilon = 0.52$ eV) is similar to spin-up/down $\pi_\perp^*$.

FIG. 3 (color online). Projected DOS of O$_2$ at bridge (a) and fcc hollow (b) sites on Pt (111) surface. Fermi energy is zero and spin-down states are plotted as negative. Isosurfaces of the real part of Bloch eigenfunctions Re($\psi_{nk}$) at $\mathbf{k} = \frac{1}{2} \mathbf{k}_0$ of the first Brillouin zone are plotted for certain unoccupied peaks, as labeled in each subfigure. The absolute isovalue for all the isosurfaces are 0.04 eÅ$^{-3}$.

Opposite in sign. Hence, our new interpretation of O$_2^*$ electronic structure is: when O$_2$ is adsorbed at bridge site of Pt(111) surface, about half electron transfers from $\pi_\perp^*$ spin-up orbital to $\pi_\perp^*$ spin-down orbital so that O$_2^*$ is nonmagnetic and also almost neutral. The transfer of electron occupation from metal to the molecule is only a “second-order” process relative to the “first-order” intramolecular spin transition.

Further analyses of the projected density of states (PDOS) of O$_2^*$ and associated molecular orbital (MO) character of the Bloch eigenfunctions $\psi_{nk}$ confirm our new interpretation. We plot the isosurface of the periodic part of Re($\psi_{nk}$) corresponding to peaks in PDOS of O$_2^*$, as indicated by arrows in Fig. 3. For O$_2^*$ at bridge site, beside the strong peak of unoccupied spin-down $\pi_\perp^*$ [labeled as $\psi_2$ in Fig. 3(a)], the spin-up or -down $\pi_\perp^*$ [$\psi_1$ and $\psi_3$ in Fig. 3(a)] states are seen to be half occupied. At fcc site, there are also a large number of unoccupied states (spectral strength) just above the Fermi level, which can be clearly identified as having $\pi_\parallel^*$ [labeled as $\psi_2$ and $\psi_3$ in Fig. 3(b)] and $\pi_\perp^*$ [$\psi_2$ and $\psi_4$ in Fig. 3(b)] character. We also integrate the PDOS below the Fermi level for both O$_2^*$ and isolated O$_2$ molecule with the same bond length as its adsorbed state. It is found that compared with isolated O$_2$, there are only slight changes in the occupied PDOS integral for adsorbed O$_2$ (from 9.57e to 9.75e for O$_2^*$ at bridge site, and 9.50e to 9.73e for O$_2^*$ at fcc site), which also suggests no large electron transfer from Pt to oxygen.
FIG. 4 (color online). Electron transfer $\Delta N$ and induced dipole $P_z$ of $\text{O}_2^-$ at bridge site versus (111) surface work function of different metals. The bond length of $\text{O}_2^-$ and its distance to the top surface layer are fixed as the optimized values on Pt(111).

The next question is whether this small charge transfer during $\text{O}_2$ adsorption is just a special case for Pt(111) surface or a prevalent phenomenon on different metal surfaces. So we have used the same method to calculate the charge transfer and induced dipole moment when $\text{O}_2$ is adsorbed at the (111) surface bridge site of several other fcc metals with different work functions, as shown in Fig. 4. Although the tendencies of increasing charge transfer and induced dipole with decreasing work function are very clear, it is found that even for Al, which is very active and easy to lose electron, $\Delta N$ is only about 0.2$e$. This result is consistent with a previous DFT calculation [19]. Under no circumstances can surface-adsorbed $\text{O}_2^-$ be classified as a true integer anion [5]. Recently, Raebiger et al. found that transition metal impurities inside bulk ionic or semiconducting crystals maintain nearly constant local charge during redox [20]. Here, we demonstrate a similar phenomenon in molecular adsorptions on metal surfaces. Both challenge conventional notions of literal integer charge transfer between adsorbates or impurities and crystals.

In conclusion, ab initio calculations reveal that $\text{O}_2^-$ adsorbed on a variety of metal surfaces possesses very little net charge and induced dipole. An intramolecular spin transition occurs when the molecule approaches the metal surface. So the adsorption energy and charge state of this important reaction intermediate are only weakly dependent on the electrode potential. The normal range of ORR cathode potential $V$ is 0.6–1.0 volt with respect to the standard hydrogen electrode (SHE) and the potential of zero charge for Pt(111)-aqueous 0.1 M HClO$_4$ interface is about 0.2 volt versus SHE [21]. Suppose half of this interfacial potential variation physically localizes within the Helmholtz plane, usually 3 Å in thickness, the predicted variation in adsorption energy due to electrostatic effect will be $\sim 10$ meV, smaller than $k_B T$. Additional calculations under strong external field ($\pm 0.5$ volt/Å) confirm that there are only small changes in both electron transfer and induced dipole moment, indicating small second-order (polarizability) effects [22]. The near-neutrality of reaction intermediates, and thus validated, enables one to greatly simplify the analysis and modeling of ORR electrocatalysis [12] for a wide range of electrode potentials.

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