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Low hole polaron migration barrier in lithium peroxide

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We present computational evidence of polaronic hole trapping and migration in lithium peroxide (Li$_2$O$_2$), a material of interest in lithium-air batteries. We find that the hole forms in the $\pi^*$ antibonding molecular orbitals of the peroxide (O$_2^-$) anion, and that this trapped hole induces significant local lattice distortion, forming a polaron.

Our study finds migration barriers for the free polaron to be between 68 and 152 meV, depending on the hopping direction. This low barrier suggests that this material might not be as insulating as previously assumed, provided that the formation of carriers can be achieved. One transport limitation may arise from lithium vacancies, which we find to strongly bind to the polaron. This result, in combination with previous experimental results, suggests that electronic conductivity in this material is likely to be determined by vacancy diffusion.

Our hypothesis is that as occupation of these $\pi^*$ orbitals influences the O–O bond strength, these states can hold a polaron.

To verify this hypothesis, we performed first-principles calculations using the Vienna Ab Initio Simulation Package (VASP) within the projector augmented-wave approach. A plane-wave energy cutoff of 500 eV and a Γ-centered $k$-point grid were used for all computations. Supercells of $3 \times 3 \times 2$ times the hexagonal unit cell of Li$_2$O$_2$ (Ref. 9) were used to minimize the interaction between periodic images. Given the large size of our supercells, we expect the energies to be fairly well-converged despite the minimal $k$-point grid used.

HSE correctly predicts stoichiometric Li$_2$O$_2$ to be an insulator with a large band gap of 4.2 eV, consistent with the previous findings of Hummelshøj et al. The relaxed lattice parameters are $a = 3.13$ Å and $c = 7.60$ Å, in excellent agreement with the experimental structure determined by Föppl et al. and verified by Cota et al. The peroxide O–O bond length in the relaxed structure is calculated to be 1.50 Å.

The polaron calculations were performed using the same methodology as outlined in our previous work. Briefly, a $\pi^*$ hole polaron is formed by removing an electron from the fully relaxed supercell, with overall charge neutrality preserved via either a compensating background charge (“free” polaron) or a compensating lithium vacancy (“bound” polaron). The supercell dimensions in the polaron calculation were fixed at the fully relaxed lattice parameters of stoichiometric Li$_2$O$_2$. We found that regardless of the type of polaron, an initial small perturbation must be applied to one
of the peroxide species and its neighboring lithium atoms to
due to polaron formation. Without this initial perturbation,
the supercell relaxes to a local minima whereby the hole is
delocalized throughout the crystal with no polaron formation.
For the “free” polaron case, this nonpolaronic supercell is
120 meV higher in energy than the supercell containing a
hole polaron localized on one of the peroxide anions. For the
“bound” polaron case (discussed later), the nonpolaronic cell
is 262 meV higher in energy than the polaronic supercell.
Hence, it is clear that proper symmetry breaking needs to
be applied when studying the electronic structure of these
defected or doped systems. We also calculated the “barrier”
of the perturbation required to transit from the metastable
nonpolaronic state to the polaronic state for the “free” polaron case, and we found it be extremely small at approximately
20 meV, which is well accessible via thermal fluctuations at
room temperature.

For the polaronic peroxide species, we find that the O−O
peroxide bond length decreases to 1.36 Å during relaxation,
which is intermediate between the nonpolaronic peroxide bond
length of 1.50 Å and the molecular oxygen O=O double bond
length of 1.27 Å. This result is in line with our hypothesis that
an antibonding electron is removed to form the hole polaron,
resulting in the contraction of the O−O bond length due to
the strengthening of the bond. At the same time, we find that
the average distance between the nine nearest neighbor Li⁺
and the midpoint of the peroxide anion increases from 2.35 to
2.48 Å, due to the decreased electrostatic interaction between
the Li⁺ and polaronic O₂⁻ species (as opposed to O₂⁻).

Further evidence of hole polaron formation can be found
in the calculated density of states (DOS), given in Fig. 2. A
clearly visible oxygen hole state can be observed just above
the Fermi level (expanded in the inset). We also note that hole-
doped Li₂O₂ is not a band conductor, and no metallic states
are present in the valence band. Although Fig. 2 shows the
DOS for the free polaron case, the DOS for the bound polaron
case is qualitatively similar. This result is in stark contrast
to the previous results of Hummelshøj et al.,2 who observed
metallic states in the valence band in the presence of lithium
vacancies. We speculate that Hummelshøj et al.’s conclusions
were based on DOS calculated for the nonpolaronic structure;
our calculated DOS for the nonpolaronic supercell is similar
to that calculated by Hummelshøj et al. and showed metallic
states near the Fermi level. However, as we noted earlier, this
nonpolaronic structure has significantly higher energy than the
polaronic structure, and we believe our polaronic structure to
be representative of the true ground state. We note that recent
work by Garcia-Lastra et al. 20 also identified strong excitonic
and vibronic effects in the optical properties of Li₂O₂, which
also suggest possible hole localization in this material.

Finally, we also plot in Fig. 3 a cross section of the
difference in calculated charge densities between the polaron-
containing supercell and a neutral supercell with the same
lattice parameters and atomic positions. The differential charge
density shows a clear localization of hole charge density on
a peroxide species, and the polarization on the surrounding
Li²⁺ ions. We note that the extent of the polarization does not
extend significantly beyond the lattice constant, which means
that the π⁺ hole polaron in Li₂O₂ is a small polaron.

To determine if the π⁺ hole polaron in Li₂O₂ is mobile,
we calculated the polaron migration barriers for hopping
between nearest-neighbor peroxide anions. The paths consid-
ered are indicated in Fig. 3. Both intralayer hops between
two nearest-neighbor peroxide anions in the same layer

FIG. 1. (Color online) Structure of Li₂O₂ and molecular orbital
(MO) diagram of peroxide anion (O₂⁻).

FIG. 2. (Color online) Density of states for Li₂O₂ containing a
free-hole polaron. Red (gray) indicates the contribution from the
oxygen atoms, while blue (dark gray) indicates the contribution from
the lithium atoms.
Intra−layer hop

in Li2O2 in the peroxide layer (red circles) and between the peroxide layers (blue squares).

(hopping distance ≈3.13 Å) and interlayer polaron hops between two neighboring peroxide anions in different layers (hopping distance ≈4.12 Å) were considered [see Fig. 3]. If we denote the initial and final ion positions as \( \{ q_i \} \) and \( \{ q_f \} \), respectively, the migration of the polaron can then be described by the transfer of the lattice distortion over a one-dimensional Born−Oppenheimer surface, with an energy maximum at a configuration between \( \{ q_i \} \) and \( \{ q_f \} \). To determine this maximum, we computed the energies for a set of cell configurations \( \{ q_i \} \) linearly interpolated between \( \{ q_i \} \) and \( \{ q_f \} \), i.e., \( \{ q_i \} = (1-x)\{ q_i \} + x\{ q_f \} \), where \( 0 < x < 1 \). We note that the polaron migration barriers calculated using these linearly interpolated coordinates are maximum values. However, while there could be paths with slightly lower energy, we do not expect them to be significantly lower.

The calculated migration barriers for a free \( \pi^+ \) hole polaron in Li2O2 are given in Fig. 4. Surprisingly, our calculations show that free polaron migration barriers in Li2O2 are extremely low, with an interlayer migration barrier of 68 meV and an interlayer migration barrier of 152 meV. As a basis for comparison, our calculated hole polaron migration barriers for the olivine LiFePO4 and LiMnPO4 cathode materials using the same HSE functional and similar parameters are 170 and 303 meV, respectively.21 These results suggest that if hole polarons can be formed in Li2O2, these holes are expected to be relatively mobile. We also expect polaronic conductivity to be anisotropic in this material, with more facile migration within the \( a-b \) layers than in the \( c \) direction. Assuming the same prefactor (even though the necessary vibrational modes for polaron migration are different in the two cases), our calculated barriers predict approximately 180 times slower polaron interlayer migration compared to intralayer migration.

We also calculated the polaron migration in the presence of Li\(^+\) vacancies (\( V_{Li^+} \)). In Li2O2, lithium vacancies can be formed in either of two symmetrically distinct sites: a Li site that is in the same layer as the peroxide anions (intralayer vacancy) or at a Li site that is between peroxide layers (interlayer vacancy). Our HSE calculations predict a Li vacancy formation energy of 3.8 eV for an intralayer vacancy and 4.1 eV for an interlayer vacancy at the bulk lithium chemical potential (the energy of metallic Li as the reference), which is somewhat higher than the 2.85 eV calculated by Hummels\textsc{h} et al. using semilocal functionals.2 We believe that the HSE functional provides a better handling of the self-interaction errors inherent in this system, as was demonstrated in other systems as well.15

Figure 5 shows the calculated barriers for polaron migration from a site nearest to the Li\(^+\) vacancy to another site nearest to the Li\(^+\) vacancy (hop coordinate from 0 to 1), and then to a site farther away (hop coordinate from 1 to 2). In general, we find that the \( \pi^+ \) hole polaron in Li2O2 is strongly bound to lithium vacancies, as expected. We may also observe that the intralayer polaron-\( V_{Li^+} \) pair is much more strongly bound than the interlayer pair, which is probably due to the fact that the polaron-\( V_{Li^+} \) distance for the intralayer pair is much shorter than that for the interlayer pair.

Using nudged elastic band methods, Chen et al.21 have calculated a barrier for \( V_{Li^+} \) migration of 360 meV, which suggests that \( V_{Li^+} \) diffusion should be relatively facile. Given the significantly lower formation energy of the intralayer vacancy (compared to the interlayer) and the strong binding of the hole polaron to such vacancies, we believe that electronic conductivity is likely to be controlled by \( V_{Li^+} \) diffusion in this system, and that conductivity takes place mainly via a polaron-\( V_{Li^+} \) pair migration through this material. Electronic conductivity should therefore be relatively high in defected
Li$_2$O$_2$. Previous experimental work by Lu et al.\textsuperscript{22} has provided speculation that nonstoichiometric and defective Li$_2$O$_2$ is formed during discharge, which could mean that electronic conductivity might not be as limiting to the performance in lithium-air batteries.

In summary, we present evidence of possible polaronic hole trapping in lithium peroxide (Li$_2$O$_2$), a material of interest in lithium-air batteries. We postulate and demonstrate that the hole forms in the $\pi^*$ antibonding molecular orbitals of the peroxide (O$_2$\textsuperscript{2-}) anion, and that this trapped hole induces significant local lattice distortion, forming a polaron. We calculate very low free polaron migration barriers in this material of 68 meV for intralayer hops and 152 meV for interlayer hops. When Li vacancies are present, the hole polaron can be strongly bound to them. The lowest energy vacancy in Li$_2$O$_2$ is formed by removing a Li in the same layer as the peroxide anions, and the resulting polaron binds to this vacancy with a binding energy of around 468 meV. Our results, therefore, suggest that electronic conduction in this material is likely to be controlled by the vacancy diffusion, which has been previously calculated to be relatively facile with a barrier of 360 meV. In conclusion, we believe that although the electronic conductivity of this material would be highly anisotropic, this material might not be as insulating as previously assumed, particularly in nonstoichiometric, defective Li$_2$O$_2$.

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