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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_2O_2), a material of interest in lithium-air batteries. We find that the hole forms in the π^* antibonding molecular orbitals of the peroxide (O_2^{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.

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Lithium peroxide (Li_2O_2) is a material of interest in lithium-air batteries.[1] During operation, it is one of the products formed on the air cathode. It has been widely speculated that Li_2O_2 is insulating, and that its electronic conductivity could become rate-limiting during charge or discharge.[2,3] In recent work,[2] Hummelshøj *et al.* calculated that Li_2O_2 is a large band-gap insulator, with a gap of 1.88 eV in semilocal density functional theory (DFT) and a gap of 4.91 eV in the more accurate G_0W_0 approximation. However, Hummelshøj *et al.* also reported computations that show that the presence of lithium vacancies induces the formation of holes in the valence band and Li_2O_2 becomes a band conductor. It was further claimed that during charge, the charging potential would result in the formation of bulk Li vacancies, the facile diffusion of which would result in electronic conductivity, while during discharge, there would always be metallic surface states due to the presence of surface vacancies.

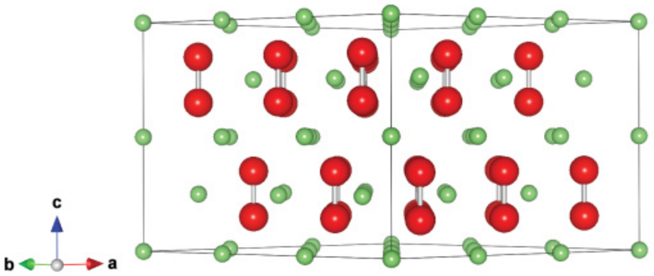
In this paper, we postulate an alternative π^* hole polaron conduction mechanism in Li_2O_2. A polaron is a quasiparticle formed by a charge and its self-induced distortion in an dielectric crystal. In recent years, the Holstein model for polaron motion[4,5] has attracted renewed interest because experimental evidence supports the presence of polaron carriers in strongly correlated electronic materials, including colossal magnetoresistance manganites,[6] organics, quasi-one-dimensional systems, and high-T_c cuprates.[7] To the best of our knowledge, this work is the first demonstration of the possibility of polaronic conduction in a peroxide species.

The structure of Li_2O_2 (Refs. 8 and 9) is given in Fig. 1(a). Li_2O_2 crystallizes in a $P63/mmc$ hexagonal space group where the peroxide anions are arranged in an alternating ABAB stacking. There are two distinct Li^+ sites: one is in the same layer as the peroxide anions and the other resides between peroxide layers. At first glance, it would appear that polarons are unlikely to form in a lithium-oxygen system, which lacks the *d* orbitals present in many correlated systems. However, one crucial difference between Li_2O_2 and a typical oxide is the presence of highly localized electrons in the covalent bonds of the O-O peroxide anions. Figure 1(b) shows the molecular orbital diagram of the O_2^{2-} peroxide species and the fully occupied antibonding π^* orbitals as the highest filled orbitals. Our hypothesis is that as occupation of these π^* orbitals influences the O−O bond strength, these states can hold a polaron.

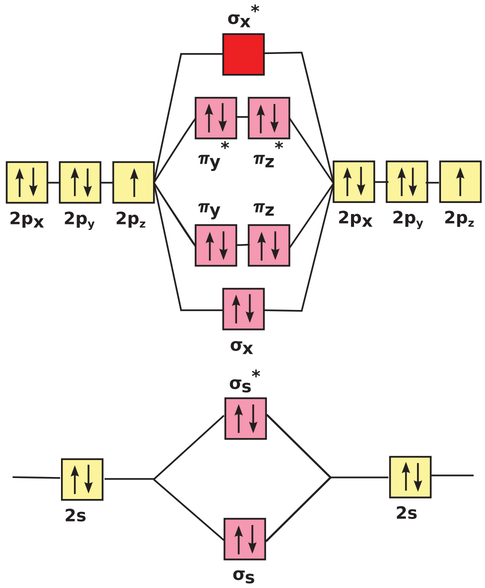
To verify this hypothesis, we performed first-principles calculations using the Vienna Ab Initio Simulation Package (VASP)[10] within the projector augmented-wave approach.[11] It is a well-known drawback of semilocal density functionals that they tend to over-delocalize electrons due to the sizable self-interaction errors.[12] Hence, all calculations were performed using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional,[13,14] which mixes a fraction of nonlocal Hartree-Fock exchange to semilocal exchange. The screened hybrid HSE functional has been demonstrated to provide a more accurate treatment of solids, particularly in the study of electron-transfer reactions, than standard semilocal DFT functionals.[15,16] This functional has similarly been used to study polaron hole trapping in the doped $BaBiO_3$ *s*-*p* system.[17] A plane-wave energy cutoff of 500 eV and a Γ-centered $1 \times 1 \times 1$ *k*-point grid were used for all computations. Supercells of $3 \times 3 \times 2$ times the hexagonal unit cell of Li_2O_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_2O_2 to be an insulator with a large band gap of 4.2 eV, consistent with the previous findings of Hummelshøj *et al.*[2] 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.*[8] and verified by Cota *et al.*[9] 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.[18,19] Briefly, a π^* 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_2O_2. We found that regardless of the type of polaron, an initial small perturbation must be applied to one



(a)Structure of Li_2O_2.



(b)MO diagram of peroxide anion.

FIG. 1. (Color online) Structure of Li_2O_2 and molecular orbital (MO) diagram of peroxide anion (O_2^{2-}).

of the peroxide species and its neighboring lithium atoms to induce 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 to 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 O_2^- species (as opposed to O_2^{2-}).

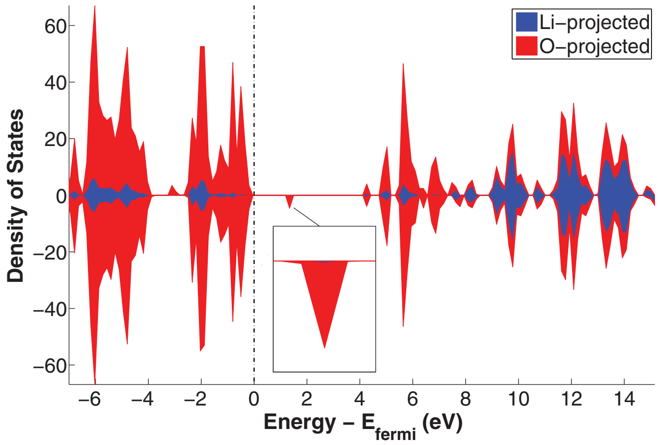


FIG. 2. (Color online) Density of states for Li_2O_2 containing a free-hole polaron. Red (gray) indicates the contribution from the oxygen atoms, while blue (dark gray) indicates the contribution from the lithium atoms.

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 Li_2O_2 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 Li_2O_2, 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 Li^+ 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 Li_2O_2 is a small polaron.

To determine if the π^* hole polaron in Li_2O_2 is mobile, we calculated the polaron migration barriers for hopping between nearest-neighbor peroxide anions. The paths considered are indicated in Fig. 3. Both intralayer hops between two nearest-neighbor peroxide anions in the same layer

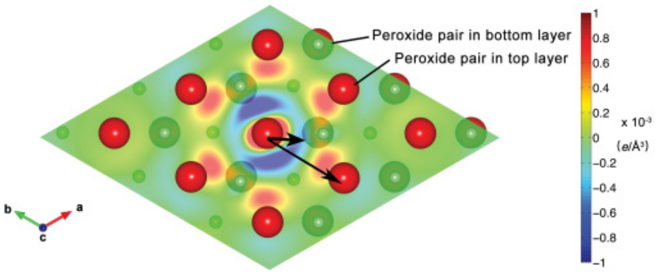


FIG. 3. (Color online) Cross section of the differential charge density between the polaron-containing cell and a neutral cell for the π^* hole polaron in Li_2O_2. Oxygen atoms are in red (dark gray), and lithium are in green (light gray). The cross section is taken in the plane bisecting the polaronic peroxide O−O bond. The polaron migration paths that were considered in this study are also indicated by the black arrows.

(hopping distance $\approx$3.13 Å) and interlayer polaron hops between two neighboring peroxide anions in different layers (hopping distance $\approx$4.12 Å) were considered [see Fig. 3]. If we denote the initial and final ion positions as $\{\mathbf{q}_\mathbf{i}\}$ and $\{\mathbf{q}_\mathbf{f}\}$, 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 $\{\mathbf{q}_\mathbf{i}\}$ and $\{\mathbf{q}_\mathbf{f}\}$. To determine this maximum, we computed the energies for a set of cell configurations $\{\mathbf{q}_\mathbf{x}\}$ linearly interpolated between $\{\mathbf{q}_\mathbf{i}\}$ and $\{\mathbf{q}_\mathbf{f}\}$, i.e., $\{\mathbf{q}_\mathbf{x}\} = (1-x)\{\mathbf{q}_\mathbf{i}\} + x\{\mathbf{q}_\mathbf{f}\}$, 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 π^* hole polaron in Li_2O_2 are given in Fig. 4. Surprisingly, our calculations show that free polaron migration barriers in Li_2O_2 are extremely low, with an intralayer 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 $LiFePO_4$ and $LiMnPO_4$ cathode materials using the same HSE functional and similar parameters are 170 and 303 meV, respectively.[19] These results suggest that if hole polarons can be formed in Li_2O_2, 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 Li_2O_2, 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 Hummelshøj *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 π^* hole polaron in Li_2O_2 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

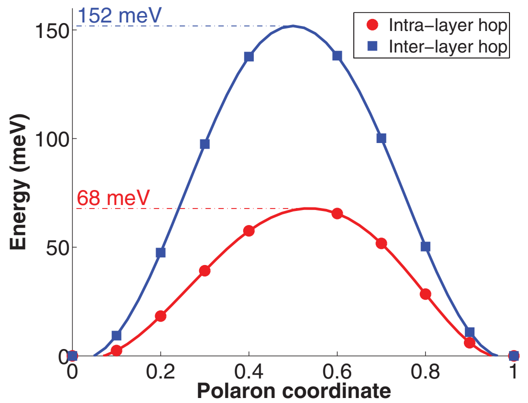


FIG. 4. (Color online) Migration barrier for free π^* hole polaron in Li_2O_2 in the peroxide layer (red circles) and between the peroxide layers (blue squares).

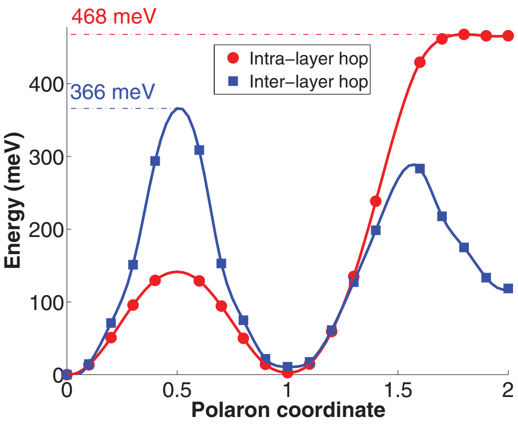


FIG. 5. (Color online) Binding energies for π^* hole polaron to V_{Li^+} vacancy in Li_2O_2.

Li_2O_2. Previous experimental work by Lu *et at.*[22] has provided speculation that nonstoichiometric and defective Li_2O_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_2O_2), a material of interest in lithium-air batteries. We postulate and demonstrate that the hole forms in the π^* antibonding molecular orbitals of the peroxide (O_2^{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_2O_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_2O_2.

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