Improving Li_2O_2 conductivity via polaron preemption: first principles study of Si doping

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Lithium peroxide Li_2O_2 is the main discharge product forming at the cathode of Li-air batteries. As the discharge process proceeds, an Li_2O_2 film grows at the cathode site, and the bulk conducting properties of Li_2O_2 begin to rate limit the transfer of electrons from the cathode to the film-electrolyte interface. As Li_2O_2 is a bulk insulator, this poor conductivity problem eventually leads to the death of the battery discharge process. This effect presents a significant problem in practical implementation of otherwise extremely perspective Li-air batteries.

Recent theoretical studies have demonstrated that stoichiometric Li_2O_2 is a wide-band-gap insulator and that charge transport in this compound takes place via polaron hopping [1-3], featuring significantly high hopping barriers [4]. Possible hole-type carriers were also shown to collapse in localized "hole-polaron" states [3].

In this study we propose an alternative way to improve the conductivity of lithium peroxide. By means of *ab initio* calculations, we show that the substitution of a small fraction (1.6%) of Li atoms by Si impurities leads to the creation of additional conducting states in Li_2O_2. These states are shown to originate from the partial occupation of oxygen antibonding orbitals by electrons donated by impurity Si atoms. The elongated oxygen pairs forming these states are bound to Si impurities and form molecular-orbital impurity states in the band gap of the system near the valence band maximum.

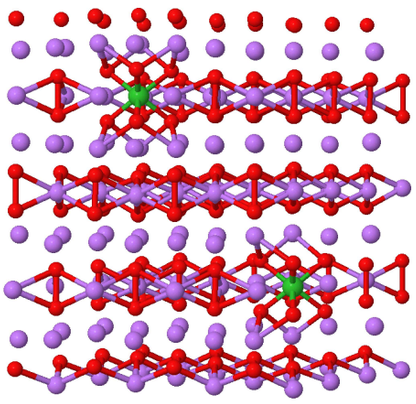

Figure 1. The 4x4x2 supercell of Li_2O_2, used in doping calculations. Li, O, and Si atoms are shown in blue, red, and green colors, respectively. The positions of Si atoms correspond to a uniform impurity distribution, used in the electronic structure analysis.

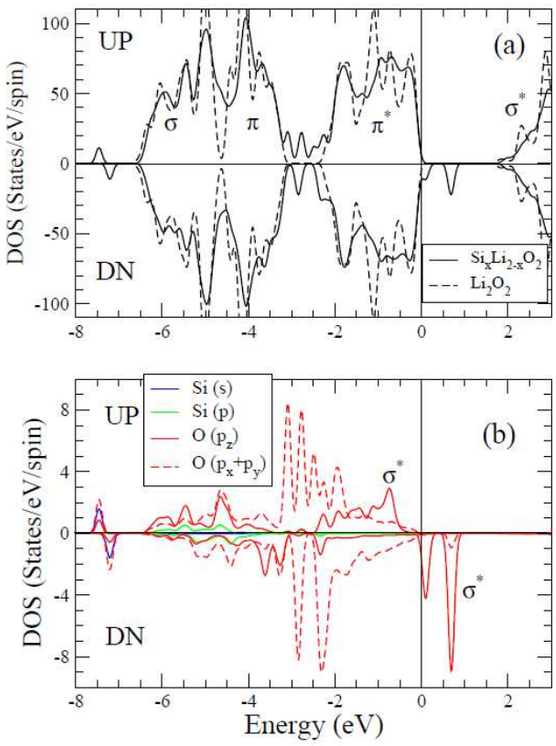

Figure 2. Panel (a) shows density of electronic states (DOS) for Si-doped Li_2O_2 256-atom supercell. DOS for undoped supercell is also shown for comparison. Panel (b) shows DOS, projected on the atomic orbitals of silicon and on the neighboring three elongated O-O pairs.

Additional electrons inserted into the Si-doped Li_2O_2 occupy these impurity states rather than forming polaronic O_3^- states at oxygen molecules not coordinated by Si. Due to their low energy position, these states are intended to capture an extra electron injected in the system before it can occupy the higher-lying intrinsic conducting states of Li_2O_2. Having accommodated an extra electron, these states are safe against any polaronic formation since any further deformation of the oxygen pair is energetically quite costly.

The conduction process is then realized by electron tunneling between O_2 ligands of Si dopants, which is predicted to enhance significantly the electron mobility of lithium peroxide. We speculate that even a small increase in the Si concentration should lead to further increase of the spacial density of conducting orbitals, leading to the formation of an intrinsic conducting network inside the Li_2O_2 crystal.

References

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