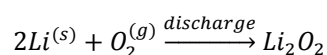


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論 文 内 容 要 旨

The aim of this thesis is to investigate the charge transport properties of lithium peroxide (Li_2O_2), which is the dominant discharge product of lithium air batteries (LAB), by carrying out first principles calculations. The concept of metal-air batteries means using the oxidation of metal with oxygen in the ambient air to produce electricity. The most remarkable advantage of metal-air batteries results from the battery setup that instead of storing the oxygen cathode in the battery it comes from the outside air. In this way, the energy density can be greatly improved. Thanks to the light weight of lithium metal, LAB provide the highest theoretical specific energy density among all the metal-air battery chemistries. Based on the oxidation of lithium pure metal, the gravimetric energy density of LAB is calculated to be 11430Wh/kg (excluding O_2 mass), which is comparable to that of gasoline (13000 Wh/kg). Since the demonstration of the first rechargeable LAB in non-aqueous electrolyte by Abraham and Jiang in 1996, LAB have now drawn increasing research interests during the last two decades as a new generation of batteries for long distance electric vehicles. However despite the promising advantage and considerable research efforts devoted to the development of LAB, there are still many severe technical as well as scientific challenges regarding to the practical application of LAB, e.g. high overpotential, low electronic energy efficiency, low rate capability etc. Among all of the factors, the charge transport limit within Li_2O_2 is one of the most important issues.

For rechargeable LAB in non-aqueous electrolyte, the dominant discharge product is Li_2O_2 according the following electrochemical reaction:



During discharge process Li_2O_2 is formed on the surface of porous electrode, and a possible reaction path proposed by J. S. Hummelshøj et al. suggested the continuous growth of Li_2O_2 is achieved by formation of Li_2O_2 on the preformed Li_2O_2 deposits. Based on this reaction scenario, the electron conductivity from the surface of electrode and that within Li_2O_2 is essential for the performance of LAB. However, since bulk Li_2O_2 is

an insulator, during the discharge process once it fully covers the surface of electrode, the charge transport process would become the rate limiting factor of the battery performance.

In the recent two decades, there have been many research papers regarding the charge transport properties in Li_2O_2 , and different mechanisms have been proposed theoretically. However a well accepted theory has not yet been achieved. Detailed and systematical investigations about the different factors that might affect the conductivity of Li_2O_2 are also quite few. Moreover, due to the high reactivity of Li_2O_2 with the surrounding environment as well as under electron beam radiation, direct experimental measurement about the charge transfer mechanism within Li_2O_2 is quite difficult.

Thus in this study, we employed the first principles calculation approach to investigate the defect and interface induced conductivity in Li_2O_2 . We focus on the defective and interfacial properties of Li_2O_2 to explore their effects on the conductivity. The calculations are divided into four parts, including the benchmark bulk properties, the intrinsic point defects, the extrinsic doping effects, and finally the interfacial properties between Au and Li_2O_2 . The whole thesis is organized as following:

General introduction emphasizes the importance and advantage of LAB as a new generation of batteries for long-distance electric vehicles, and lists the organization of this current thesis.

Chapter 1 introduced the working mechanism of LAB, discussed the existing challenges and problems related to the practical application of LAB, and reviewed the literature work about the charge transport mechanism of Li_2O_2 . Motivated by the above contents, we focused this current Ph.D work on the exploration of the conductivity of Li_2O_2 . The objectives of this study are to investigate the defective and interfacial properties relevant to the conductivity of Li_2O_2 .

Chapter 2 presents a brief illustration of the many-body problem, density functional theory (DFT) together with the different forms of exchange correlation approximations including LDA, GGA and Hybrid DFT theory, as well as the many-body GW approximation. With the progress in computational hardware, computational physics also experienced a rapidly development. Especially, first principles calculation has been proved to be a very successful method to study the geometric, energetic, electronic and many other properties of materials. Now the density functional theory (DFT) based on W. Kohn theorems and Hedin's GW approximation (GWA) are demonstrated to be the most successful approaches to treat the ground state and excited state of many-body systems respectively. DFT is the simplest and most effective quantum mechanical modeling method available in physics and chemistry now. However it greatly underestimate the bandgap of semiconductors and insulators. Hybrid DFT methods improve the results by partially incorporated Hartree-Fock exact exchange, while GW approximation is now the most accurate method for bandgap calculation by involving the many-body electron-electron interaction. Thus for the bulk calculation of Li_2O_2 , we presented a detailed comparison of the bulk bandgap calculated by applying standard DFT, hybrid DFT, as well as the state-of-the-art many-body GW approximation to give a reliable estimation of its bandgap. The supercell method for charged point defects calculations and the slab method for interfacial calculation are also explained.

Chapter 3 carried out benchmark calculation of the bulk properties of Li_2O_2 . We started from its crystal structure, following by the electronic structure, especially the evaluation of its bandgap. Previous study has demonstrated that bulk Li_2O_2 is an insulator, however no experimental measurement of the bandgap value is

available until now. Since the bandgap is important for our prediction of its other properties, in this part of study, different calculation techniques have been devoted to predict its bandgap. GGA-PBE, HSE06 and GW0 approximation based on GGA and HSE06 initial wavefunctions have been carried out.

Our calculated results show that the structure of bulk Li_2O_2 contains an array of highly covalent O_2^{-2} molecular anions and a matrix of Li^+ cations, and PBE and HSE06 gives slightly different lattice constants. The electronic structure of Li_2O_2 is mainly dominated by the molecular orbital of O_2^{-2} peroxide anion, which greatly determines the following defective and interfacial properties. Bulk Li_2O_2 is a large bandgap insulator. PBE, HSE06 and GW0 calculations result in quite different bandgap values. The PBE and HSE06 results are consistent with the literature values, while the GW0 results lays just in between the previous G0W0 and scGW calculations. Our HSE06 based GW0 result gives a bandgap value of more than 6.50 eV. However due to the large computational cost of GW approximation, it is now suitable for the following defective and interface calculation. Therefore, as a common practice, in the following part of this thesis, for the defect properties we adapted the lattice constants calculated by HSE06, and adjusted the mixing parameter α in HSE06 to be 0.5 in order to get a bandgap value of 6.50 eV, which is close to our HSE06-GW0 related results and also comparable to previous treatment of the bandgap.

Chapter 4 investigated the intrinsic point defects in Li_2O_2 , including different types of small polarons (electron and hole polaron) and vacancies (Li vacancy, O vacancy and di-O vacancy) at different charge states. The formation energy, transition level, and binding energy between different defects were calculated. The electronic structure, defect levels as well as the defects induced conductivity were discussed in detail. The supercell method with 144 atoms ($3 \times 3 \times 2$) was used, and a compensating background charge was introduced to the system for the charged point defects. The Freysoldt correction scheme was applied for the correction of imaging charge interaction as well as the electrostatic potential alignment. The dielectric constants were evaluated to be around 10 for the Freysoldt correction.

The calculated results demonstrated that the intrinsic defective properties of Li_2O_2 are controlled by the ability of O_2^{-2} peroxide anion to change its charge states through the formation of electron and hole polarons. The most stable neutral and negative defects in Li_2O_2 are the neutral O vacancy and negative Li vacancy respectively. Other charge states of these two vacancies are corresponding to formation of additional electron and hole polarons. Polaron hopping and Li vacancy migration are supposed to be the dominating charge transfer mechanisms related to intrinsic Li_2O_2 . This conclusion is consistent with other literature works. The calculated conductivity related these two mechanisms are consistent with the low conductivity in Li_2O_2 .

Chapter 5 gives a systematical investigation of the extrinsic defective properties in Li_2O_2 , including the effect of intended metal/semimetal doping and behavior of unavoidable hydrogen impurity. Light elements including Na, Mg, Al, Si, K, Ca in the second and third period from group I to group IV were introduced to bulk Li_2O_2 to substitute Li atom. And hydrogen atom was considered to be both an interstitial and substitutional impurity at Li, O and di-O sites. The same $3 \times 3 \times 2$ supercell was used and the impurity concentration is around 0.7 at% percent.

The calculated results show that for metal/semimetal doping in Li_2O_2 , except for Na and K, other metal/semimetal doping is favorable to be formed with negative formation energies. And the formation energy decreases as the increase of the valence electrons, and increases upon increase of the atomic radius of

dopant atom. Si doping results in the lowest formation energy on both T- and O-site Li. Besides, multi-electron polarons will be formed next to the doping atom due to electron donation from the additional valence electrons to the antibonding O-Pz states of O-O peroxide anion. And the formation of electron polarons is supposed to stabilize the doping system. However as the highly localized defect levels form deep acceptor levels, and they can hardly be effective to improve the conductivity of Li_2O_2 . Moreover, the defect levels are highly depended on the calculated bandgap. Upon bandgap opening, these doping induced gap states shifted to much higher energy levels. For hydrogen atom as an impurity, it can be easily incorporated into Li_2O_2 as an interstitial impurity. The bonding between interstitial hydrogen and O_2^{2-} peroxide anion results in electron donation from H 1s to O-Pz orbital to form a three-center bond of O-H-O or O-O-H. Hydrogen substitution of lithium and oxygen forms complexes of hydrogen with negative lithium vacancy and the hydroxyl-like species, respectively. Both types of hydrogen impurities electrically counteract with the prevailing conductivity of Li_2O_2 , making it an unwanted impurity in the application of LAB. Thus so far, our calculation proposed that doping in Li_2O_2 will not be a wise strategy to improve its conductivity. Some alternative methods, like the interface induced conductivity etc., are needed to be further investigated.

Chapter 6 calculated the interface properties between Au and Li_2O_2 , which is derived by the experimental conditions that nanoporous gold is used as the electrode for cathode of LAB. Other than a quite simply interface model used in previous literature papers, a systematical comparison of the coherent and semicoherent interface configurations was carried out. The detailed interfacial atomic configuration, charge transfer mechanism, electronic structure change upon interface formation has been investigated in detail. The strain induced artificial effect in the coherent interface case was discussed, and the effect of the gold substrate on the conductivity of Li_2O_2 was emphasized. Periodic slab model formed between Au (111) and Li_2O_2 (0001) was used for the calculation. Both Li-terminating and O-terminating Li_2O_2 (0001) surface were considered. Different binding positions of Li_2O_2 on Au at T, B, H sites for coherent type and different superlattice of Li_2O_2 overlayer on Au substrate were calculated.

The calculated results show that for both configurations, the formation of interface between Au and Li_2O_2 will introduce conduction states between the valence and conduction band of Li_2O_2 . These states are from the Au d states, which fill the gap between O-Pxy and O-Pz orbitals, resulting in conductivity. The affinity and charge transfer between Au/Li-terminating interface and Au/O-terminating system are different because of the polar nature of both Au and Li_2O_2 (0001) surfaces. Compared to the coherent interface configuration, the semicoherent case can greatly reduce the strain energy. And the ultimate difference between Li-terminating and O-terminating interfaces can be obtained in the more realistic semicoherent configuration. Au-Li binding at the interface region will gradually shift the O states of the adjacent O-O layer to lower energy levels, consequently decrease the bandgap of the Li_2O_2 , while the weak interaction between the both negatively charged Au-O layers results in almost no change in the electronic structure of Li_2O_2 .

Chapter 7 gives the final conclusion of this Ph.D work and summarizes the main results of each part of calculation.

論文審査結果の要旨

リチウム空気電池は、質量あたりのエネルギー密度が 10,000 Wh/kg 以上あり、次世代の蓄電池として有望視されている。電池内にアノード電極側に Li 金属、カソード電極側に触媒電極(Au など)を設置し、リチウムの酸化還元反応： $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ を利用して放電・充電する仕組みである。原理は単純であるが、技術的に困難な面が指摘されている。それは、生成される過酸化リチウム(Li_2O_2)が電氣的絶縁性であることが挙げられる。しかし、過酸化リチウムの基礎物性がほとんどわかっておらず、改善のための手がかりが掴めないでいるのが現状である。過酸化リチウムは大気中で不安定な化合物であり、実験が困難な面があるため、第一原理計算によって正確な電荷移動特性を計算することが望まれている。そこで、康 利静氏は、第一原理を駆使することで、過酸化リチウムの電荷移動特性についての包括的な研究をおこなった。

論文は7つの章で構成されており、概要は以下のとおりであった。

第1章：リチウム空気電池の科学的背景

リチウム空気電池の概要とそのボトルネックについての詳細が記述された。

第2章：第一原理計算の理論的背景

正確な物性を予測するための第一原理計算(DFT)の詳細な条件について検討した。

第3章：過酸化リチウムのバルクでの電荷移動特性

固体 Li_2O_2 の結晶構造の計算結果、電子状態(DOS)、バンドギャップの定量的な評価を行った。

第4章：結晶欠陥による過酸化リチウムの電荷移動特性

点欠陥の種類(Li 空孔、酸素空孔、酸素 2 重空孔)、その形成エネルギー、局所電子状態について評価した。

第5章：異種元素ドーピング過酸化リチウムの電荷移動特性

アルカリ金属(Na, Mg, Al, Si, K, Ca)と水素ドーピングによる結晶構造の変化、電荷移動の変化の評価をおこなった。

第6章：金／過酸化リチウム界面での電荷移動特性

Au との整合界面、準整合界面の原子模型の構築と、界面近傍での局所電荷分布や電子状態についての評価をおこなった。

第7章：結言

簡潔に結果がまとめられた。

このように、本論文は過酸化リチウム(Li_2O_2)の第一原理計算による詳細な検討と結果が示されており、その達成度と独自性は極めて高く評価できる。また、このような第一原理計算による詳細な検討は、康利静氏の高い専門知識と独自性により構築・展開されたものであり、研究者としての極めて高い資質を示している。

よって、本論文は博士(工学)の学位論文として合格と認める。