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研究论文

锂在共轭双键高分子中的电化学嵌入反应III. 锂嵌入聚噻吩的量子化学计算†

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摘要 采用Gaussian软件和HF方法, 通过从头计算(*ab initio*)法选取4-31G基组计算锂离子嵌入聚噻吩过程中结构与结合能的变化关系. 发现噻吩聚合时主要生成三或四聚合物. 聚合物在Li原子(或Li^+离子)嵌入后, 聚噻吩间距离明显变小, 同时发生电荷转移, 形成稳定嵌合物; 并使噻吩环的C-*α*—C-*β*键级变小. 同时, 研究了锂离子(或原子)嵌入后体系的HOMO, LUMO能级. 聚噻吩在嵌入锂离子时LUMO轨道能级变为负值, 成为电池反应得电子的正极. 而金属Li_2释放Li^+后的Li^-的HOMO能级为＋0.7427 eV, 则成为给电子的负极. 由此, 可以完成由锂/聚噻吩在高氯酸锂电解质中组成的放电过程, 并提出嵌合键级概念用来表征锂在聚噻吩间的结合程度.

关键词 嵌合物 键级 嵌合键级 电池反应

分类号

Electrochemical Intercalation Reaction of Lithium in the Macromole-cule with the Conjugate Double-bond III. Quantum Chemical Calcu-lation for Intercalation of Lithium into the Polythiophene†

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Abstract Using Gaussian and HF, via *ab initio* method and selecting 4-31G basis set, the transformation connection between the structure and binding energy was investigated in the process of lithium ion interca-lating into polythiophene. And when the thiophene polymerized, it was found that tri-polymer or tetra-polymer were main products. As the intercalation of lithium atom (or Li^+ ion) into the polymer, the distance between the polythiophenes was shortened obviously. At the same time, the intercalation substances became stable due to the electric charges transferring, which made bond order of the C-*α*—C-*β* decreased in the thiophene. The HOMO, LUMO energy level of the system was calculated when the lithium ion (or atom) intercalated into. The LUMO orbit energy level of polythiophene turned negative with the lithium ion intercalating into, and became the positive pole of the cell reaction that received electron. While after the metal Li_2 released Li^+, the HOMO energy level of Li^- was 0.7427 eV, and became the negative pole which was given electron. Thus, the discharge process of lithium/polythiophene was finished in the electrolyte of the lithium perchlorate. It was also indicated that the conception of the intercalation bond order was used to denote the combination degree of lithium between the polythiophene.

Key words intercalated compound bond order intercalated bond order cell reaction

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