第63回応用物理学会春季学術講演会 講演予稿集 (2016 東京工業大学 大岡山キャンパス)

Mechanism of Interaction of Li with Tetracyanoethylene (TCNE) and Tetracyanoquinodimethane (TCNQ): Promising Materials for Organic Batteries

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Tetracyanide molecules such as tetracyanoethylene (TCNE) and tetracyaniquinodimethane (TCNQ) have been proposed as promising candidate materials for organic battery electrodes, including lithium ion as well as sodium ion batteries. Their high theoretical capacities are in particular due to the possibility to store more than one alkali atom per molecule. Here, we present a density functional theory study of lithium attachment to TCNE and TCNQ. Trends in the Li binding strengths (which determines the electrode voltage) are presented between TCNE and TCNQ and a function of the number of attached Li atoms. We show that multiple Li attachment induces non-trivial changes in the electronic structure. Electron donation from Li/Na is possible to higher (than LUMO) unoccupied molecular orbitals as well as Li-centered orbitals. Strain effects induced by Li attachment lead to significant changes in the electronic structure and can induce changes in orbital ordering. A cyclic structure stabilized by Li attachment to TCNE is identified. We conclude that design of organic electrode materials should consider the energies of higher (than LUMO) orbitals as well as effects of structural changes on the electronic structure.

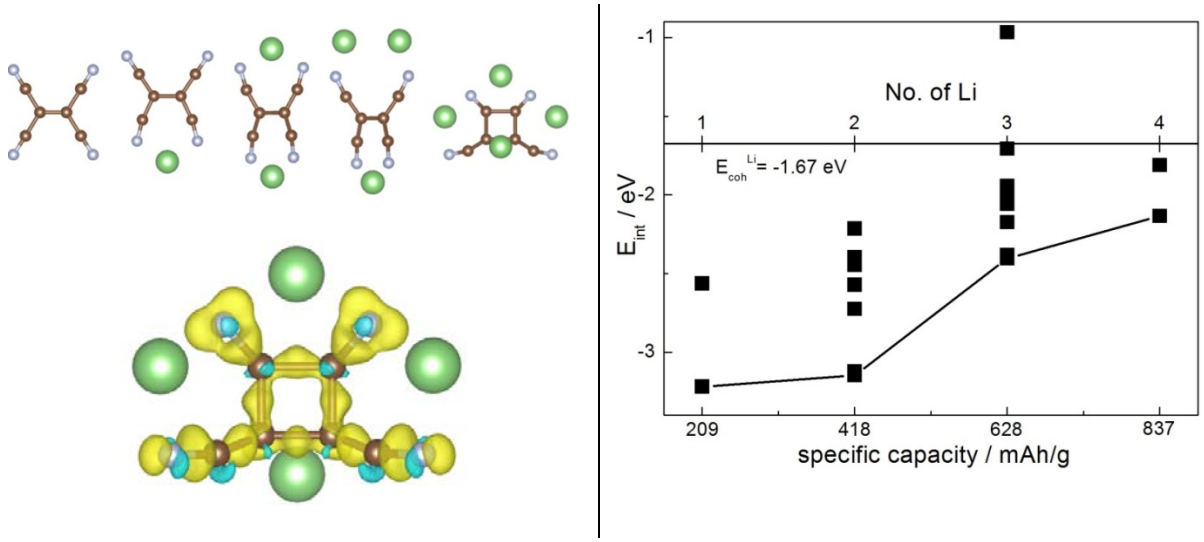

Figure 1. *Left: the TCNE molecule and lowest-energy Lin-TCNE complexes, n=1…4. Atom colour scheme here and elsewhere: C – brown, N – blue, Li – green, H – pink. Below, charge density difference between the total electron density of a Li_4-TCNE complex and the sum of atomic densities is shown, evidencing the C-C bond formation by density accumulation along the bond. Right: The interaction energies of Li with TCNE, per Li atom, in Lin-TCNE complexes. The line connects the lowest energy structures while symbols correspond to all identified stable structures. The axis showing No. of Li atoms crosses the energy axis at the cohesive energy of Li, -1.67 eV.*