

## 科学研究費助成事業 研究成果報告書

平成 28 年 6 月 13 日現在

機関番号：11301

研究種目：若手研究(B)

研究期間：2014～2015

課題番号：26800220

研究課題名(和文) Charge transport inside of organic crystals and lithium-containing metal oxides

研究課題名(英文) Charge transport inside of organic crystals and lithium-containing metal oxides

研究代表者

Packwood Daniel (Packwood, Daniel)

東北大学・原子分子材料科学高等研究機構・助教

研究者番号：40640884

交付決定額(研究期間全体)：(直接経費) 1,100,000円

研究成果の概要(和文)：[1] 確率モデルの分析を行い、有機結晶中の電子の移動が高相関性を有する分子間振動に強く依存することが分かり、有機結晶の電気的特性の説明を提案した。[2] C60結晶のMDシミュレーションをベース統計で分析し、分子間のHOMO-LUMO相互作用のためのメカニズムを提案した。[3] LiCoO<sub>2</sub>中のLiイオンの拡散を、六方格子上的ランダムウォークとして研究した。結晶格子の異なる部分での同時から生じるLi移動がLiイオンの拡散に対するエントロピー障壁を生成することが分かった。

研究成果の概要(英文)：[Part 1] Electrons in organic crystals become less mobile with temperature (A) and are highly localized (B). A stochastic model showed that charge transport in organic crystals depends upon correlated intermolecular vibrations. The weakening of this correlation with temperature explains (A). The localization of correlated vibrations explains (B). [Part 2] We analysed MD simulations of C60 crystals using Bayesian statistics and discovered a new mechanism for electronic coupling between C60 molecules. Here, the HOMO of one C60 molecule is modulated by its vibrations and the vibrations of a neighboring C60 molecule. The HOMO then excites more vibrations within the molecules, which then modulates the LUMO energy of the neighboring molecule. [3] We analysed Li<sup>+</sup> ion diffusion in LiCoO<sub>2</sub> by studying random walks on a hexagonal lattice. We found that an entropy barrier to Li<sup>+</sup> diffusion which arises from simultaneous, localized Li<sup>+</sup> motion in different parts of the crystal lattice.

研究分野：物理化学

キーワード：Organic semiconductors Metal oxides Lithium ion batteries Bayesian networks

## 1. 研究開始当初の背景

Organic semiconductors are widely expected to replace silicon in some next-generation electronics. Charge transport in organic semiconductors has two unique features: charge mobility that decreases with temperature, and a charge that is localized to within a few unit cells. The former feature is typical of band transport as seen in metals, in which scattering of charge carriers becomes more important as temperature increases. However, the latter property does not fit within the band transport picture, in which charge carriers are very delocalised. The charge transport mechanism in organic semiconductors is therefore controversial and cannot be described by typical models.

Lithium-containing metal oxides (LMOs) such as  $\text{LiCoO}_2$  are used as anode materials in lithium ion batteries. In LMOs, the  $\text{Li}^+$  ion hops between sites (octahedral sites between  $\text{CoO}_2$  layers in  $\text{LiCoO}_2$ ) in the crystal with a diffusion rate determined by hopping activation energies and the arrangement of hopping sites in the crystal. At present, there is much effort in understanding the physical mechanism that determines the activation barriers to hopping, however there appears to be relatively little work into understanding how the arrangement of hopping sites affects  $\text{Li}^+$  transport properties.

## 2. 研究の目的

**Goal A.** To characterize charge transport in organic semiconductors by considering the pathways for charge carriers through the semiconductor.

Elucidation of charge transport mechanisms in organic semiconductors will enable the fabrication of organic semiconductors with improved electrical properties. To the best of my knowledge, there has been no attempt to connect the charge transport properties of organic semiconductors with the specific pathways that charge carriers follow in the crystal.

**Goal B.** Identify  $\text{Li}^+$  transport paths which slow down the diffusion rate of  $\text{Li}^+$  in LMOs.

If we can identify paths which slow down the rate of  $\text{Li}^+$  transport in LMOs, then we can prevent these  $\text{Li}^+$  ion from using these

paths by careful design of the materials. To the best of my knowledge,  $\text{Li}^+$  ion transport kinetics have not been studied from the point-of-view of transport pathways before.

## 3. 研究の方法

### Goal A. Organic semiconductors

We used two methods for studying charge transport in organic semiconductors. In Method 1, we considered a 2D crystal containing  $N$  molecules. The dynamics of a single excited electron was studied with the tight binding model with stochastic couplings (the ‘stochastic tight binding’ / STB model). These stochastic couplings model the intermolecular vibrational (phonon) modes in the crystal. The STB model was then studied with the perturbative expansion. With the perturbative expansion, we can study the wave function of the electron as a superposition of charge transport ‘pathways’.

In Method 2, we performed ab initio molecular dynamics simulations on a FCC crystal of  $\text{C}_{60}$  molecules. We then analyzed these results using Bayesian network analysis, and identified how the coupling between the HOMO of one molecule and the LUMO of another molecule is mediated by a sequence of intramolecular vibrations.

### Goal B. Lithium-containing metal oxides

$N$  random walks on a finite hexagon lattice was considered as a model for  $\text{Li}^+$  diffusion in  $\text{LiCoO}_2$ . We analysed the state space of this model, where a single state corresponds to one way of placing the  $N$  random walks on the lattice. The diffusion speed (the time taken for  $\text{Li}^+$  ions to reach their equilibrium distribution) was estimated by taking a large sample of subsets of states from the state space and then calculating the ‘conductivity’ of each subset. The subset with the smallest conductivity is called the ‘Cheeger subgraph’. The Cheeger subgraph describes the motion of the  $\text{Li}^+$  ions during the rate-determining step for  $\text{Li}^+$  ion equilibration in  $\text{LiCoO}_2$ .

#### 4. 研究成果

##### Goal A: Organic semiconductors

###### *Results from method 1*

Numerical simulation of the STB model for an anthracene crystal correctly predicted the temperature dependence of the charge mobility and high charge localization. This demonstrates the adequacy of the STB model for studying charge transport in organic semiconductors.

Mathematical analysis of the perturbative expansion showed that only certain charge transport paths make a significant contribution to the charge transport wave function. In particular, the important charge transport paths are those in which the intermolecular vibrational modes are highly correlated in both space and time. This shows that charge transport in organic semiconductors is strongly dependent on correlated intramolecular vibrational motions. We could then deduce the following facts.

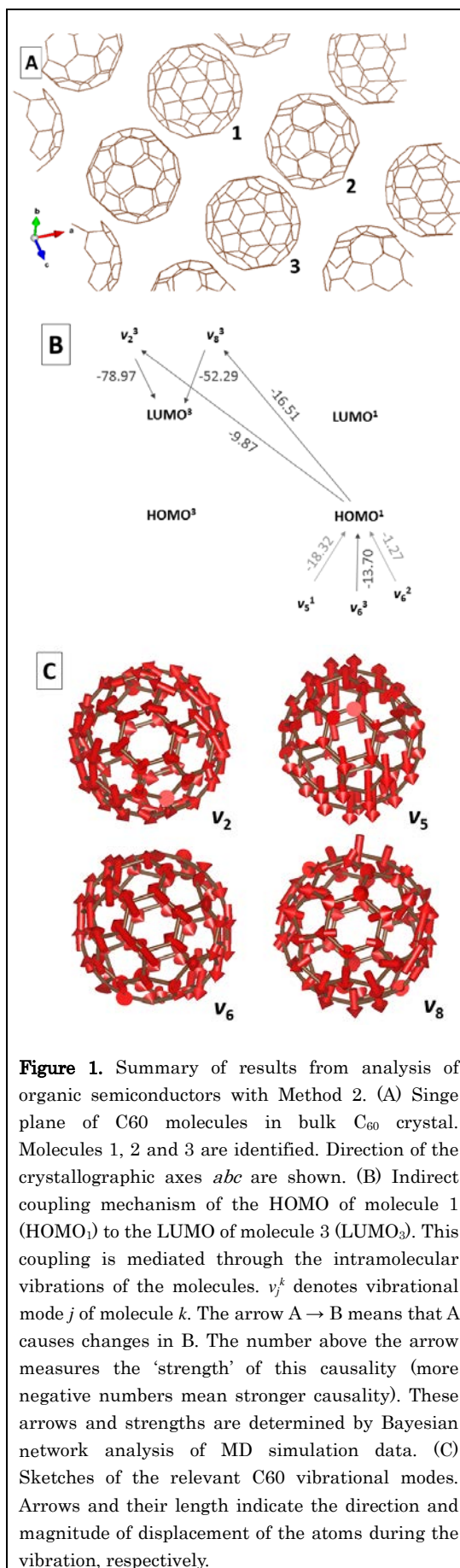
(i) Because the correlation of the vibrational modes weakens with temperature, charge mobility decreases with temperature.

(ii) Highly correlated vibrational modes must be close together in space; vibrational motion at one part of the crystal will not be correlated with vibrational motions in another, far separated region of the crystal. Because of the spatial localization of correlated vibrational motion, the charge becomes localized.

Following (i) and (ii), we describe the charge transport mechanism in organic semiconductors as a 'correlation-dependent charge transport'. This study was published in this study in the *Journal of Chemical Physics*.

###### *Results from method 2*

Method 2 considers charge transport in  $C_{60}$  crystals. Analysis of an ab initio molecular dynamics simulation using Bayesian networks identified a mechanism for coupling the HOMO and LUMO orbitals of different molecules in the crystal (Figure 1). In this mechanism, the energy of the HOMO orbital of one  $C_{60}$  molecule is modulated by the intramolecular



**Figure 1.** Summary of results from analysis of organic semiconductors with Method 2. (A) Single plane of  $C_{60}$  molecules in bulk  $C_{60}$  crystal. Molecules 1, 2 and 3 are identified. Direction of the crystallographic axes  $abc$  are shown. (B) Indirect coupling mechanism of the HOMO of molecule 1 ( $HOMO_1$ ) to the LUMO of molecule 3 ( $LUMO_3$ ). This coupling is mediated through the intramolecular vibrations of the molecules.  $v_j^k$  denotes vibrational mode  $j$  of molecule  $k$ . The arrow  $A \rightarrow B$  means that  $A$  causes changes in  $B$ . The number above the arrow measures the 'strength' of this causality (more negative numbers mean stronger causality). These arrows and strengths are determined by Bayesian network analysis of MD simulation data. (C) Sketches of the relevant  $C_{60}$  vibrational modes. Arrows and their length indicate the direction and magnitude of displacement of the atoms during the vibration, respectively.

vibrational motion of the surrounding molecules. The HOMO then causes other

vibrational motion in the surrounding molecules, and this motion then modulates the LUMO energy of the surrounding molecules. These vibrations involve global (rather than local) deformations of the C<sub>60</sub> molecules, such as rotations and axial compressions. This mechanism therefore gives an indirect coupling of the HOMO orbitals of one molecule and the LUMO orbitals of the surrounding molecules.

To the best of my knowledge, this is the first time such an HOMO-LUMO coupling mechanism has been detected in the organic semiconductor literature. This coupling may contribute a charge transport pathway between molecules in a C<sub>60</sub> crystal, however further study is necessary to clarify this point. If this coupling mechanism is important in charge transport, then these results will provide a molecular level-understanding of the physics involved in the charge transport paths. This understanding would go beyond the more general concept of ‘correlations’ described in Method 1, and would provide hints for synthesizing molecules to improve charge transport.

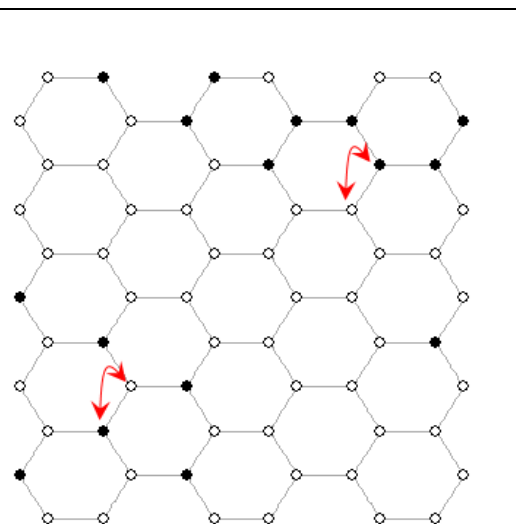
A paper on this study is currently under preparation.

### Goal B. Lithium-containing metal oxides

Our analysis suggested that the rate-determining step for Li<sup>+</sup> equilibration in LiCoO<sub>2</sub> crystals involves simultaneous, localized rearrangements of the Li<sup>+</sup> ions in different parts of the crystal (Figure 2). This probably corresponds to an entropy barrier to Li<sup>+</sup> ion equilibration, however further analysis is needed for verification.

To improve Li<sup>+</sup> diffusion speeds, we therefore need to reduce the occurrence of simultaneous, localized rearrangements in the crystal. This might be obtained by reducing the width of the crystal compared to its length. This would allow for transport pathways in which local Li<sup>+</sup> rearrangements occur mainly in one direction only, and these should have a lower entropy of activation. We will check this hypothesis by performing calculations on hexagonal lattices with a narrow width and long length.

Before publishing this result, we must improve our method for detecting the ‘Cheeger subgraph’ mentioned in the



**Figure 2.** Motion of the Li<sup>+</sup> ions (black points) between octahedral sites in the LiCoO<sub>2</sub> lattice (white points) as the system passes through the rate-determining step to equilibration of Li<sup>+</sup> diffusion in the crystal. The rate determining step involves simultaneous, localized rearrangements of the Li<sup>+</sup> ions (red arrows) in separated parts of the lattice. Further work is needed to verify the accuracy of this result, and to elucidate the physical nature of this rate-determining step (i.e., the kind of barrier that it represents).

methods section. The state space for this model is extremely big, and it is not clear if the analysis has yielded the correct result. As a next step, I will employ an ‘information reduction’ technique developed in other research to reduce the size of the state space. I expect this to be complete within the next 3 months.

### 5. 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

[雑誌論文] (計 1 件)

Daniel M. Packwood, Kazuaki Oniwa, Tienan Jin, Naoki Asao. Charge Transport in Organic Crystals: Critical Role of Correlated Fluctuations Unveiled by Analysis of Feynman Diagrams. *Journal of Chemical Physics* 142, 2015, 144503 – 144514. (査読有)

[学会発表] (計 3 件)

Daniel M. Packwood, Charge Transport Inside of Organic Crystals: The Crucial Role of Correlated Fluctuation. *AIMR-NCTU Joint Workshop on Fusion of*

*Mathematics, Nano-Materials, and Nano-Devices*, National Chiao Tung University, Hsinchu, Taiwan (22 September 2014) [Invited oral presentation]

Daniel M. Packwood, Charge Transport Inside of Organic Crystals: The Crucial Role of Correlated Fluctuations. *RIMS International Conference: Mathematical Challenge to a New Phase of Materials Science*, Masukawa Hall, Kyoto University, Kyoto (7 August 2014) [Invited oral presentation]

Daniel M. Packwood, Charge Transport Inside of Organic Crystals Studied with a Cycle Expansion Method, *AIMR International Symposium*, Sendai International Conference Center, Sendai (17 February 2014) [Invited Oral presentation]

[図書] (計 0 件)

[産業財産権]

○出願状況 (計 0 件)

名称：  
発明者：  
権利者：  
種類：  
番号：  
出願年月日：  
国内外の別：

○取得状況 (計 0 件)

名称：  
発明者：  
権利者：  
種類：  
番号：  
取得年月日：  
国内外の別：

[その他]  
ホームページ等

6. 研究組織

(1) 研究代表者  
パックウッドダニエル (PACKWOOD, Daniel),  
東北大学・原子分子材料科学高等研究機構・  
助教

研究者番号：40640884

(2) 研究分担者  
( )

研究者番号：

(3) 連携研究者  
( )

研究者番号：