

論文の内容の要旨

Development of Nanostructured Liquid-Crystalline Ion Conductors for Photovoltaic Applications

(太陽電池への応用のためのナノ構造液晶イオン伝導体の開発)

ホグベーリ ラルス ダニエル オスカー

1. Introduction

Self-assembled materials consisting of organic molecules have attracted a great deal of attention for application in energy devices. In particular, liquid crystals with well-defined nanopathways for the transport of ions are prospective as electrolytes to replace standard liquid electrolytes. Applying liquid crystals in electrochemical devices such as lithium batteries and dye-sensitized solar cells (DSSCs) may solve fundamental issues associated with liquid electrolytes such as leakage and evaporation. The objective of this thesis is to design and synthesize physically robust and thermally stable ion conductors. This new class of electrolytes will be applied in DSSCs, and their performance in operating devices will be evaluated.

The thesis consists of 4 main chapters. Chapter 2 focuses on the development of a new type of liquid-crystalline electrolyte and its application in DSSCs. Chapter 3 explores on the advantageous thermal behavior of DSSCs containing liquid crystals. Chapter 4 & 5 focuses on how molecular design can be used to alter the behavior and properties of the electrolytes and the final devices.

2. Results and Discussion

Chapter 2. The aim of this chapter is to design rod-like mesogens that show thermally stable LC phases and exhibit high ion-mobility with the aim to develop durable DSSCs. With this goal in mind, a new two-component LC electrolyte, consisting of the carbonate-based mesogenic molecule **1** and the ionic liquid (IL) **PMII** (Figure 1), has been developed. The electrolyte (**1/PMII**) is composed of **1** and **PMII** (20 mol% of I₂) in a 40:60 mol % (**1:PMII**) ratio. The **1/PMII** mixture exhibits a layered smectic A (Sm A) LC phase from 0 to 108 °C and the IL was found to be incorporated inside the layered nanostructure. The ion conductivities were measured parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the layers. The value of σ_{\parallel} is $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at 40 °C is about 4.5 times higher than the value of σ_{\perp} ($4.8 \times 10^{-5} \text{ S cm}^{-1}$). These results suggest that **1/PMII** exhibit anisotropic ion conduction in the LC state. The LC electrolyte was applied in DSSCs and the initial devices showed a power conversion efficiency (PCE) of 2.2 % at 60 °C.

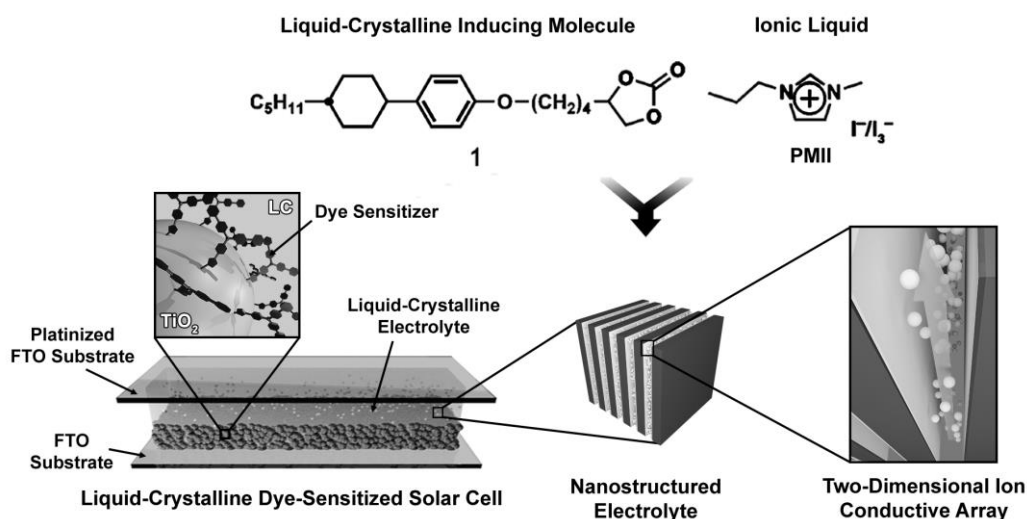


Figure 1. Conceptual image of nanostructured material consisting of molecule **1** and ionic liquid **PMII**.

The performance of the **1/PMII** DSSCs were improved (from 2.2% to 3.9% at 60 °C) by increasing the thickness of the TiO₂ film used as working electrode. Furthermore, the type of dye-sensitizer significantly affect the performance of the LC-DSSCs. It was found that the **1/PMII** device show higher PCE when using organic dyes as compared to standard ruthenium based metal-complexes. The best PCE of 5.2 % was obtained with an indole-based dye (**D205**). In contrast, the standard ruthenium dye **N719** showed a PCE of 2.2 %. This difference was traced to lower electron density in the working electrode of the **N719** device, indicating problems with electron injections. It is proposed that the high concentration of iodides in the nanostructured channels results in reductive quenching of the excited **N719** molecules, competing with the electron injection.

Chapter 3. The aim in this chapter is to develop DSSCs that can operate efficiently at elevated temperatures and to evaluate the device performance as a function of temperature. In order to achieve this, solar cells based on the liquid crystal **1/PMII** have been studied as a function of temperature and compared with reference cells containing only **PMII**. The **1/PMII**-devices show an increase in power conversion efficiency (PCE) on heating from 1.0 % at 30 °C to 2.7 % at 90 °C. In contrast, a decrease from 2.9 % at 30 °C to 1.5% at 90 °C was observed for the liquid **PMII**-devices. Interestingly, the **1/PMII**-DSSCs show higher PCE as compared to the IL-based device over 70 °C, even though the IL electrolyte show higher ion diffusion at this temperature. These results indicate that other factors than the mass-transport of the electrolytes play a role in the improved temperature performance of the LC-DSSC. It was found that the **1/PMII**-based cell exhibits longer TiO₂ electron life-time (τ) than the IL-based cell. The **1/PMII** device shows a slight τ decay upon heating. However, this tendency is more pronounced for the **PMII** device. These observations suggest that unwanted electron recombination reactions issues become more significant in the IL-based cell than in the LC-based DSSC at elevated temperatures. It is proposed that the polar carbonate moieties and ionic species interact with the TiO₂ surface, driving self-organization along the electrode surface, which spontaneously induces the formation of a nanostructured insulating layer around

the $\text{TiO}_2/\text{D35}$ interface. The formed layer would act as a barrier against the I_3^- species and lead to a decrease in the undesired electron recombination process.

Chapter 4. With the aim to further improve the PCE of the LC-DSSCs, a longer and more flexible oligooxyethylene spacer was introduced in the mesogen (Figure 2). The oligooxyethylene-linked mesogen was mixed with the IL **EMII** (electrolyte **2/EMII**). The mixture shows a Sm A phase from below 0 to 78 °C. Higher triiodide diffusion ($D_{\text{I}_3^-}$) was measured for the **2/EMII** electrolyte as compared to the alkyl-linked electrolyte **1/EMII**. The **2/EMII**-DSSCs show a maximum PCE of 6.1% (average 5.8%) at 30 °C. In contrast the **1/EMII**-DSSCs show a PCE of 1.6%. The oligooxyethylene linker successfully improves the PCE of the LC-based devices at lower temperatures. As temperature is increased, the device performance of the **2/EMII**-DSSCs gradually decreases. However, more than 90% of the initial PCE value (5.2%) is maintained at 60 °C. On further heating, the rate of decrease in PCE is significantly increased after the isotropization temperature of 78 °C. This indicates that the LC state of the electrolyte is important for the stable PCE at higher temperatures.

Chapter 5. Single-component mesogenic compounds covalently bonding an imidazolium moiety doped with I_2 was developed (compound **3**) with the aim to improve the thermal behavior of the LC-DSSCs. Compound **3** show a smectic A (Sm A) phase from below 0 to 180 °C, significantly wider than for the two-component analogues. LC-DSSCs containing **3** show higher PCEs than **1/EMII**-based devices above 90 °C. The maximum PCE (2.4%) of the **3**-based DSSCs was recorded at 120 °C. This is an improvement of the maximum operation temperature by 30 °C as compared to the **1/PMII**-DSSCs. These results can most likely be traced to the more thermally stable LC phase of **3**. The stability of the self-assembled nanostructures is apparently paramount to achieve stable device performance at elevated temperatures. Furthermore, the LC-DSSCs exhibit excellent long-term stability over 1000 hours at the operation temperature of 120 °C.

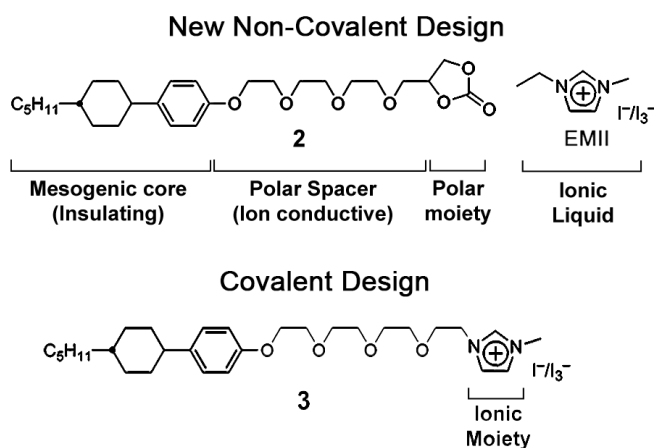


Figure 2. Molecular structure of compound **2**, **3**, and ionic liquid **EMII**.

3. Conclusion

Liquid-crystalline electrolytes that show excellent physical properties and thermal stability has been developed and applied in DSSCs. DSSCs based on the LC electrolytes show better photovoltaic performance at elevated temperature as compared to liquid-based devices. This behavior is traced to the self-assembling properties of the liquid crystals. It is also found that the LC based electrolytes are more suitable to be used together with organic dye sensitizers as compared to standard ruthenium-based complexes. Furthermore, the introduction of the flexible oligooxyethylene spacer in the mesogenic molecular design between the terminal group and the mesogenic moiety significantly improves the PCE of the LC-DSSCs. The DSSCs containing the **2/EMII** electrolytes show a maximum PCE of 6.1 %, the highest PCE reported for LC-DSSCs. In contrast, covalent-type liquid crystals show excellent high temperature stability and performance. A maximum PCE value of 2.4% was obtained at 120 °C for DSSCs containing **3**, the highest max operating temperature reported for a solar cell. In addition, DSSCs based on the LC electrolytes show excellent long-term stability over 1000 hour. These LC electrolytes opens up new paths for developing durable DSSCs that can be operated under extreme conditions. Furthermore, the robustness and the flexible molecular design of liquid crystals show their potential as a new class of electrolytes that may contribute to the development of efficient and safe energy devices.

4. Acknowledgements

First and foremost, I would like express my greatest gratitude to my supervisor, Prof. Takashi Kato, for his guidance and encouragement these past years. I would also like to express my greatest gratitude to both Prof. Hiroshi Segawa and Prof. Lars Kloo for their collaboration in this project and making this thesis possible. I would like to thank Prof. Satoshi Uchida and Prof. Masafumi Yoshio for continuously teaching me and always giving me the needed support to push the research forward. Lastly, I would like to thank all the members in both Kato laboratory and Segawa laboratory for making these past 3 years very enjoyable. I would also like to acknowledge the financial support from the Japanese Government in the form of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) scholarship.

5. References

- [1] T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno, M. Funahashi, *Nat. Rev. Mater.* **2017**, 2, 17001.
- [2] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, 110, 6595–6663.

List of Publications

1. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *Chem. Mater.* **2014**, 26, 6496–6502. *ACS Editor's Choice, Highlighted in ACS C&EN News. November 2014.*
2. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *Chem. Mater.* **2016**, 28, 6493–6500. *Selected as Journal Cover.*
3. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *ChemPlusChem* **2017**, 82, 834–840. *Selected as Journal Cover.*