





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指導教員 承認印	主	副	副
			

2019 年 12 月 5 日
Year Month Day

学位 (博士) 論文要旨
(Doctoral thesis abstract)

論文提出者 Ph. D. Candidate	生物システム応用科学府 食料エネルギーシステム科学 専攻 一貫制博士課程 平成 28 年度入学(Your Entrance Fiscal Year) 氏名 今田泰史  (Your Name(Family, First) and Seal)				
主指導教員 氏名 Chief Advisor's Name	千葉 一裕	副指導教員 氏名 Vice Advisor's Name	西河 淳	副指導教員 氏名 Vice Advisor's Name	野村 義宏
論文題目 Title	Investigation of the Effects of Electrolytes on Radical Cation Species and Electrode Materials on Anodic Oxidation of Styrenes (ラジカルカチオン種に対する電解溶液の効果とスチレンの陽極酸化への電極素材の効果の研究)				

論文要旨 (和文要旨(2000字程度)または英文要旨(500words))

※欧文・和文どちらでもよい。但し、和文の場合は英訳を付すこと。

Write a summary in Japanese (2000 characters) or in English (500words).

If the abstract is written in Japanese, needed to translate into English.

Electro-organic chemistry has received a great attention as a powerful and eco-friendly synthetic methodology. While this methodology has strong points such as sustainability, facile manipulation and scalability, one of the significant drawbacks is that there are many parameters to optimize. In particular, electrolytes and electrode materials have significant impact on reaction efficiency. Although these factors can be issues in electrochemistry, they can also be the keys to control the reactions. However, in the most cases the effects of electrolytes and electrode materials have not been disclosed. Thus, I decided to work on these two topics to illuminate their roles.

On another note, our laboratory has been developing electrochemical C-C bond formations via radical cation species. For examples, [4+2] cycloaddition (radical cation Diels-Alder reaction) and [2+2] cycloaddition were established. In both cases, electron transfer itself catalyzes them, which means that only catalytic amount of electricity is sufficient to accomplish the reactions. This will be quite important technology to exploit "electron-catalytic" reactions more and more, resulting in dramatically decreasing the consumption of reagents. However, there is a critical issue to realize it. LiClO₄/CH₃NO₂ electrolyte solution is uniquely efficient for our developed reactions via radical cation intermediates, and the reason has not been clear for the last 20 years. Therefore, the strong motivation of elucidating it made me worked on it.

It was turned out that LiClO₄, LiTFSI and LiFSI in nitroalkane have the effect of ensuring the inherent reactivity of radical cation species respectively. ⁷Li NMR studies and raman spectroscopy showed that those Li salts form the contact ion pair and/or aggregation in CH₃NO₂ solution, that is, Li cations trap the corresponding anions. It is reasoned that radical cation species could be free in those solutions like in fluorinated alcohol solutions, leading to their higher reactivities. This was supported by cyclic voltammetry studies and experiment results of electrolysis. This discovery is crucial for C-C bond formation via radical cation in electrochemical reactions. Surprisingly, this electrolyte effect had been unclear for the last 20 years.

Moreover, the newly discovered electrolyte, LiTFSI, was applied for thermomorphic media, which

enables the use of hydrophobic compounds in electrolyte and recycle of supporting electrolyte. This had not been possible with $\text{LiClO}_4/\text{CH}_3\text{NO}_2$ solution due to its high polarity. LiTFSI can be dissolved in methylcyclohexane (Me-cHex)/1-nitropropane (1-NP), which is mixable at room temperature and separable at $-50\text{ }^\circ\text{C}$. Hydrophobic products are recovered in the Me-cHex phase, and the left LiTFSI/1-NP is recyclable.

On another note, the effect of electrode materials on anodic oxidation of styrenes was also elucidated. Cyclic voltammetry studies and experiments with modified electrodes exhibited that styrenes tend to be adsorbed on the surface of carbon electrodes, leading to the better chance for dimerization. The feature enabled different functionalization of styrenes with oxygen by different electrode materials (tetrahydrofuran formation on carbon electrode and C=C cleavage on platinum electrode). On both reactions, a variety of styrene derivatives were confirmed to react smoothly.

I believe that these findings will be quite useful for further development of electrochemical reactions.

(英訳) ※和文要旨の場合(300 words)

If the abstract is written in Japanese, needed to translate into English.(300 words)