（様式 5）

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学位（博士）論文要旨

(Doctoral thesis abstract)

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論 文 題 目 (Title)	高出力・高エネルギー密度型 次世代キャパシタに向けた電解液の設計 Electrolyte Design for Next-Generation Electrochemical Capacitors with High Power and High Energy Densities

論文要旨（2000 字程度）
(Abstract(400 words))
※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。
(in English or in Japanese)

This thesis is focused on $Li_4Ti_5O_{12}$ (LTO)//activated carbon (AC) hybrid capacitors with LTO negative and AC positive electrodes as the second-generation capacitor and Li_3VO_4 (LVO)//$Li_3V_2(PO_4)_3$ (LVP) SuperRedox Capacitors (SRC) with LVO negative electrode and LVP positive electrode as the third-generation capacitor. The aim was to improve the energy density and cyclability of these capacitors through the development of electrolytes.

In chapter 1, two strategies for increasing the energy density of electrochemical capacitors, namely, higher voltage and higher energy density, were discussed along with the previous studies on the material and configuration of next-generation capacitors.

In chapter 2, the energy density of thick LTO//AC hybrid capacitors (600 μm) was improved via high ionic conductivity electrolytes. The utilization of dual-cation electrolytes constructed with a Li-based electrolyte ($LiBF_4$) and an additional supporting electrolyte (quaternary ammonium salts or ionic liquids) are a promising strategy toward simultaneously achieving thick-electrode (> 100 μm) lithium-based energy storage devices with high power and high energy densities. We observed that

1-ethyl-3-methylimidazolium tetrafluoroborate was suitable for the dual-cation electrolyte in an LTO//AC hybrid capacitor, showing 64% capacity retention at a high current density of 200 mA cm^{-2}. The EMI-based dual-cation system exhibited the highest ionic conductivity and output characteristics compared to other dual-cation systems even with lowered Li^+ transport in the bulk electrolyte.

In chapter 3, the energy density was improved *via* high-voltage operation (3.2 V~) LTO//AC hybrid capacitors using dual-cation electrolytes. H_2 gas generation with associated swelling using LTO-based hybrid capacitors upon high-voltage operation over 3.2 V has been a major challenge owing to catalytic reductive decomposition of solvent such as propylene carbonate (PC) and H_2O at the Lewis acid sites on the LTO surface. We report a method to suppress gassing behavior by adding spiro(1,1')-bipyrrolidinium tetrafluoroborate ($SBPBF_4$) to the lithium-based electrolyte [1 M lithium tetrafluoroborate ($LiBF_4$) in PC]. The dual-cation (Li^+/SBP^+) electrolyte, which has previously been reported as the electrolyte composition used for rate-capability enhancement, reduced the volume of generated H_2 to almost half of that generated using the single-cation (Li^+) electrolyte under high-voltage floating conditions (3.5 V, 60 °C). This behavior was attributed to the LTO surface passivated by the Lewis-based layer *via* Hofmann elimination of SBP^+.

In chapter 4, long-term cyclability of LVO//LVP full cell was achieved for the new-generation capacitor devices *via* optimizing the electrolyte compositions. LVO//LVP full cell are promising devices for high power and high cyclability as a result of these characteristics of the LVO negative electrode and LVP positive electrode. However, the LVO//LVP full cells that we constructed exhibited a capacity decay over 1000 cycles at 50 °C (72%) owing to large state of charge (SOC) shift, which are unique to sloping charge-discharge curves such as that of LVO. In this chapter, we clarified the capacity decay mechanism through the negative and positive capacity (N/P) ratios in LVO//LVP full cells and charge-discharge simulations. During the charge-discharge tests, the SOC shift decreased and the capacity retention increased with an increasing N/P ratio. We also applied a vinylene carbonate (VC) additive to the LVO//LVP to overcome the capacity decay at a low N/P ratio, resulting in low SOC shift and high capacity retention with the VC.

（英訳）※和文要旨の場合(400 words)