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| 氏名 | WANG ZHONG |
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| 学位論文題目 | Study on functional organogelators with electrochemical applications<br>(電気化学的応用を有する機能性有機ゲル化剤に関する研究) |
| 論文審査委員 | 主査　教授　英　謙二<br>教授　鈴木 正浩<br>教授　市川 結<br>教授　鮑 力民<br>教授　堤 宏守　(山口大学) |

# 論　文　内　容　の　要　旨

A substance is a gel, as defined by Flory, if it has a continuous structure which exhibits solid-like rheological behavior, and has macroscopic dimensions that are permanent on the time scale of an analytical experiment. Recently, low molecular weight gelators (LMWGs), which can form supramolecular gels, have attracted great attention mainly because of their unique properties and potential applications as new soft materials. LMWGs have been reported by many excellent reviews and books. Non-covalent forces such as hydrogen bonding, van der Waals, π–π stacking, and electrostatic interactions contribute to the self-assembly. LMWGs form various kinds of nanostructures, such as nanofibers, nanoribbons, nanosheets, nanoparticles, helical, and bundle structures. With a suitable solvent choice it is possible to control the LMWGs nanostructures.

The name of battery to describe a group of electronic devices was credited by Benjamin Franklin. With growing requirements of renewable energy, the demand for green lithium ion batteries is continuously increasing. The cathode materials generally used in lithium-ion batteries are inorganic materials (e.g., $LiCoO_2$, $LiMnO_4$), which have some drawbacks involving the limited theoretical capacity, unrenewable resources, and large energy consumption. Organic compounds, which can be prepared by environmentally benign processes, have been investigated for renewable resources. Their structures also allow them to be used for several different applications. Organic electroactive materials have some superior advantages, i.e., lightness, flexibility, and processing compatibility.

Electrolytes are ubiquitous and indispensable in all electrochemical devices, and their basic function is independent of the much diversified chemistries and applications of these devices. When electrodes are placed in an electrolyte and a voltage is applied, the electrolyte will conduct electricity. Lone electrons normally cannot pass through the electrolyte; instead, a chemical reaction occurs at the cathode, providing electrons to the electrolyte. Another reaction occurs at the anode, consuming electrons from the electrolyte. As a result, a negative charge cloud develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte neutralize these charges, enabling the electrons to keep flowing and the reactions to continue. Because of the physical location in the electrochemical devices, the electrolyte is in close interaction with both of anode and cathode. Traditional lithium ion battery is using polar solvent and lithium ion as the electrolyte, which usually has the advantage of high conductive, low cost, high ionic transform speed, and long cycle life. However, some challenges, such as leakage and

inflammability, exist that limit their possible applications. Solid electrolytes have also played an important role in solid-state batteries because they offer higher energy density than traditional electrolytes in normal lithium-ion batteries. However, the problems of stability, mechanical strength, cost, and environmental influences have not yet been solved satisfactorily. With regard to the shortcomings of traditional electrolytes, gel electrolytes have been widely studied. Gel electrolytes are materials that combine the properties of both liquid and solid electrolytes.

In chemistry, the radical is an atom, molecule or ion that has an unpaired valence electron. These unpaired electrons make free radicals highly chemically reactive. Nitroxides, as stable organic radicals, represent an interesting class of molecules that form the basis of novel and emerging functional materials such as radical batteries, spin probes, polarizing agents for DNP-NMR, antioxidants, magneto-active materials, and radiation protective agents owing to their single component charge-transfer properties. 2,2,6,6-tetramethyl-piperidine 1-oxyl free radical (TEMPO) is the present of the nitroxide. The four α-methyl groups of nitroxide in TEMPO work to make the radical groups stable. Among the radical polymers poly(2,2,6,6-tetramethylpiperidinyl--oxy-4-yl methacrylate) (PTMA), a derivative of polymethacrylate with a TEMPO radical in repeating unit exhibited high capacity, good rate performance and long cycle life used as a cathode material for LIBs.

With a growing demand for renewable energy, the demand for green LIBs is continuously increasing. The cathode materials generally used in LIBs are inorganic materials (e.g., $LiCoO_2$, $LiMnO_4$), which have some drawbacks related to their limited theoretical capacity, unrenewable resources, and large energy consumption. Organic compounds, which can be prepared by environmentally benign processes, have been investigated as renewable resources. Organic materials also have the advantage of diversity; different side chains or structures, so they can performance different properties though easy syntheses.

In this study, the purpose of the studies was carried out within the following aspects:

(1) Investigation of gel electrolyte.

Cyclo(L-β-3,7-dimethyloctylasparaginyl-L-phenylalanyl) was used as a gelator to synthesize gel electrolytes with 1-butyl-3-methylimidazolium tetrafluoroborate, propylene carbonate, and γ-butyrolactone in 1 M $LiBF_4$. Gel strengths and thermal stabilities were studied with respect to the effect of graphite as an additive. Ionic conductivities, activation energies for ionic conductivity, and the electrochemical stabilities of the graphite-containing gel electrolytes were also studied.

(2) Functional gelators with electrochemical properties.

Low-molecular-weight gelators bearing 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were synthesized by amidation reactions with DiC and DMAP. The gelators formed thermal-reversible gels in various organic solvents and electrolytes. The minimum gelation concentration against γ-BL containing lithium salts increased as compared to that of neat γ-BL. The increase in the minimum gelation concentration is due to the dielectric constant of γ-BL increasing as a result of addition of lithium salt. TEM images of the loose xerogel in γ-BL exhibited clear fibers with a diameter of ~100 nm, while the image of γ-BL including lithium salts showed slender fibers, suggesting the interruption of fibers growth by lithium salts. The strengths of the gels containing lithium salts decreased as compared to that of neat γ-BL, indicating that the lithium salts obstructed the growth of fibrous aggregation. Electrochemical measurements, including cyclic voltammetry and cell performances confirmed the redox properties and showed a plateau output voltage with a rapid charging-discharging process.

In this study, I prospect to manufacture a type of soft battery with organic cathode and LMWG electrolytes which has the properties of flexible and safe. This type of battery might be used on the clothes with the flexibility. There would also be no problems associated with dangerous high temperatures due to the gel-sol phase transition, which would act as a safety mechanism by preventing the battery from working.