



Design of Catalytic Reactions and Functional Materials Using Redox Properties of Metal Complexes and Organic Molecules

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Doctoral Dissertation

博士論文

Design of Catalytic Reactions and Functional Materials Using Redox

Properties of Metal Complexes and Organic Molecules

(金属錯体と有機分子のレドックス特性を用いる触媒反応と

機能性材料の設計)

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Contents

Abbreviation

General Introduction

1) Preface	1
2) Transition Metal-Catalyzed Carbon-Carbon Bond-Forming Reactions of Organosilicon Compounds	2
(a) Cross-Coupling Reactions of Organosilicon Compounds	2
(b) Organic Synthesis Using Organosilanols	9
(c) Organic Synthesis of Organosilicon Compounds Bearing Si-O Bonds	17
3) Organic Polymers for Rechargeable Batteries	25
4) Purpose and Scope	34
5) References and Notes	40

Chapter 1. Silicone as an Organosilicon Reagent for the Palladium-Catalyzed Cross-Coupling Reaction

1.1 Introduction	47
1.2 Experimental	48
1.3 Results and Discussion	55
1.4 Conclusion	73
1.5 References and Notes	74

Chapter 2. TEMPO Radical Substituted Silicones: Syntheses and Electrochemical

Properties as Active Materials for Organic Radical Batteries

2.1	Introduction	77
2.2	Experimental	79
2.3	Results and Discussion	85
2.4	Conclusion	93
2.5	References and Notes	94

Chapter 3. Cationic Polymerization of Poly(vinyl ether) Bearing a TEMPO Radical:

A New Cathode Active Material for Organic Radical Batteries

3.1	Introduction	96
3.2	Experimental	98
3.3	Results and Discussion	103
3.4	Conclusion	108
3.5	References and Notes	109

Chapter 4. Effect of Ethylene Oxide Structures in TEMPO Polymers on High-Rate

Discharge Properties

4.1	Introduction	111
4.2	Experimental	113
4.3	Results and Discussion	118
4.4	Conclusion	126
4.5	References and Notes	127

Chapter 5. Fabrication of a Practical and Polymer-Rich Organic Radical Polymer

Electrode and its Rate Dependence

5.1	Introduction	129
5.2	Experimental	130
5.3	Results and Discussion	133
5.4	Conclusion	140
5.5	References and Notes	141

Chapter 6. Summary and Prospects

6.1	Summary and Prospects	143
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List of Publications

Acknowledgement

Abbreviation

A	ampere
Ac	acetyl
acac	acetylacetonato
aq	aqueous
Ar	aryl
bp	boiling point
br	broad (in NMR)
Bu	butyl
°C	degree Celsius
calcd	calculated
cat	catalyst(s)
CMC	sodium carboxymethyl cellulose
cod	1,5-cyclooctadiene
Cy	cyclohexyl
CV	cyclic voltammetry
δ	chemical shift in parts per million downfield from tetramethylsilane (in ^1H and ^{13}C NMR)
d	doublet (in NMR)
dba	dibenzylidene acetone
DEC	diethyl carbonate
DMF	<i>N,N</i> -dimethylformamide
D ₃ ^{Ph}	2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane
D ₄ ^{Ph}	2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane
DMSO	<i>N,N</i> -dimethylsulfoxide
dppb	1,2-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
EA	elemental analysis
EC	ethyl carbonate
eq.	equation

equiv.	equivalent(s)
ESR	electron spin resonance
Et	ethyl
g	gram(s)
h	hour(s)
Hex	hexyl
HMPA	hexamethylphosphoramide
HRMS	high-resolution mass spectrum
Hz	hertz
IR	infrared
<i>J</i>	coupling constant (in NMR)
L	liter(s)
LiPF ₆	lithium hexafluorophosphate
LiBETI	lithium bis(pentafluoroethanesulfonyl)
μ	micro
m	multiplet (spectral), meter(s), milli
M	moles per liter, mega
Me	methyl
min	minute(s)
<i>M_n</i>	number average molecular weight
<i>M_w</i>	weight average molecular weight
mol	mole(s)
mp	melting point
MS	mass spectrometry
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
nbd	2,5-norbornadiene
Ph	phenyl
PMHS	poly(methylhydrosiloxane)
ppm	parts per million (in NMR)

Pr	propyl
PTFE	poly(tetrafluoroethylene)
PVdF	Poly(vinylidene fluoride)
q	quartet (in NMR)
rt	room temperature
s	singlet (in NMR), second(s)
SEC	size exclusion chromatography
SEM	scanning electron microscope
t	triplet (in NMR)
TBAF	tetra(<i>N-tert</i> -butyl)ammoniumfluoride
TEMPO	2,2,6,6-tetramethylpiperidine- <i>N</i> -oxyl
TLC	thin-layer chromatography
TMS	trimethylsilyl, tetramethylsilane
tol	tolyl
VGCF	vapor grown carbon fiber
wt	weight
XRD	X-ray diffraction

General Introduction

Abstract: Cross-coupling reactions using organosilicon compounds in the presence of a transition metal catalyst and rechargeable batteries using organic radical polymers will be reviewed.

- 1) Preface
- 2) Transition Metal-Catalyzed Carbon-Carbon Bond-Forming Reactions of Organosilicon Compounds
 - (a) Cross-Coupling Reactions of Organosilicon Compounds
 - (b) Organic Synthesis Using Organosilanols
 - (c) Organic Synthesis of Organosilicon Compounds Bearing Si-O Bonds
- 3) Organic Polymers for Rechargeable Batteries
- 4) Purpose and Scope
- 5) References and Notes

1) Preface

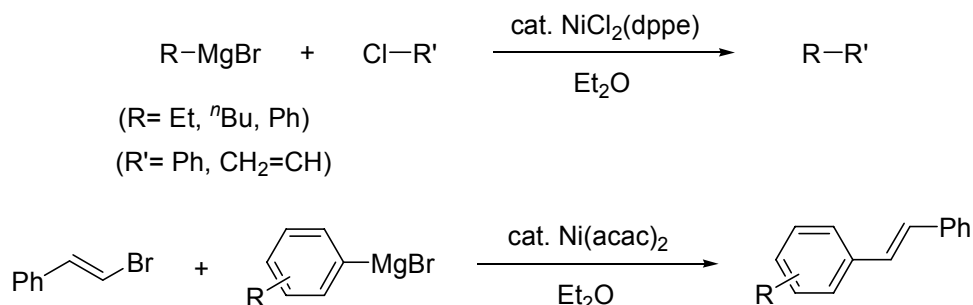
Through the present Thesis, the Author has studied new transition-metal-catalyzed reactions, redox-active polymers, and electrodes for rechargeable batteries. Development of new reactions is strongly correlated with the design of new functional materials. As the requirement for high-performance materials increases, preparation of new materials is becoming more difficult using only previously reported reactions. Accordingly, development of new materials induces development of new synthetic reactions, and these new reactions may encourage the creation of other materials. Therefore, the methodologies for both functionality and reactivity are strongly related.

Humans have recently been faced with environmental and energy-shortage problems. Without a solution to such problems, society would not be able to remain sustainable. Development of batteries, which is a key to solving our energy problem, is a major concern. This Thesis focuses on the preparation of new rechargeable batteries based on organic polymers. The preparative methodology of such materials is associated with the use of novel transition-metal-catalyzed synthetic reactions, part of which organosilicon chemistry is used. The Author would like to contribute to solving the global energy and environmental problems by development of useful devices as well as new synthetic reactions.

2) Transition Metal-Catalyzed Carbon-Carbon Bond-Forming Reactions of Organosilicon Compounds

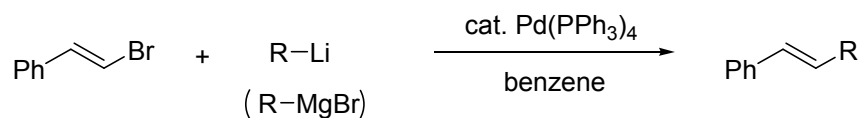
(a) Cross-Coupling Reactions of Organosilicon Compounds

Transition-metal-catalyzed cross-coupling reactions are now known as versatile carbon-carbon bond forming reactions.¹ Since Kumada and Corriu² reported a transition-metal-catalyzed reaction, a number of them have been developed (Scheme 1).



Scheme 1. First cross-coupling reaction using organometallic compounds

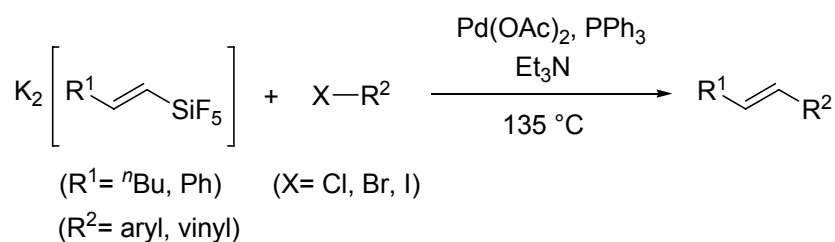
In particular, palladium complexes are one of the most effective organometallic compounds. The first palladium-catalyzed cross-coupling reaction was reported by Murahashi (Scheme 2).³ Palladium-catalyzed coupling reactions have been useful carbon-carbon bond forming reactions and have been used in the synthesis of functional materials such as pharmaceutical intermediates, agricultural chemicals, and electronic materials.



Scheme 2. First palladium-catalyzed cross-coupling reaction

As for organometallic compounds, organoboron compounds (Suzuki-Miyaura)⁴ are widely used reagents because of their high reactivity and wide functional group tolerance. However, organoboron compounds are not available for synthesis of a large quantity of products because of their high cost. In addition, organotin compounds (Migita-Kosugi-Stille)⁵ are also known as highly reactive compounds. However, organotin compounds are far from useful organic reagents because of their high toxicity. Therefore, cross-coupling reactions of organosilicon compounds⁶ as coupling reagents are being examined instead of organoboron and organotin compounds.

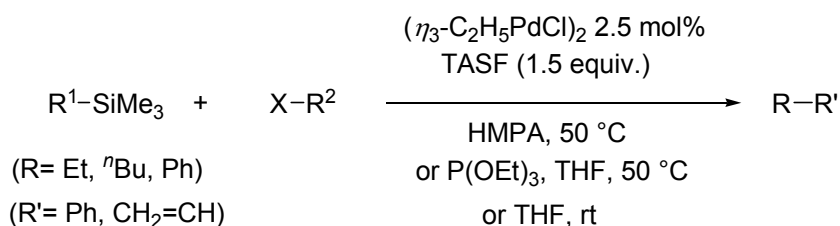
The first study of a cross-coupling reaction using an organosilicon compound was reported by Tamao-Kumada (Scheme 3).⁷



Scheme 3. First cross-coupling reaction using organosilicon compounds.

However, this organosilicon-based coupling reaction is not widespread as a synthetic tool since high-temperature and less available organosilicon compounds are required. The development of organosilicons as cross-coupling reagents has been slower than that of the other organometallic compounds because of their lower reactivity.

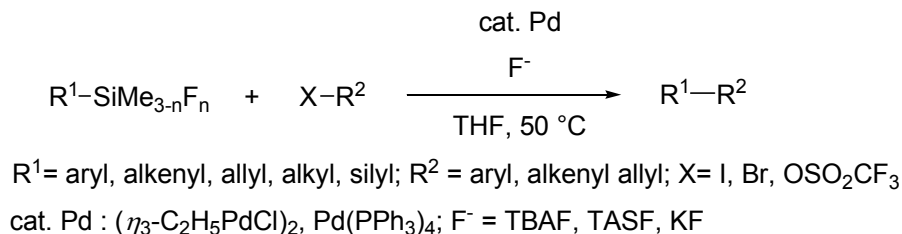
Hiyama reported that a fluoride ion activates the lower reactivity of organosilicon compounds (Scheme 4).⁸ Although this reaction is also not useful since hexamethylphosphoramide (HMPA), which is known as a highly toxic and possible carcinogenic compound, is used as a reaction solvent.



Scheme 4. Cross-coupling reactions of organosilicons.

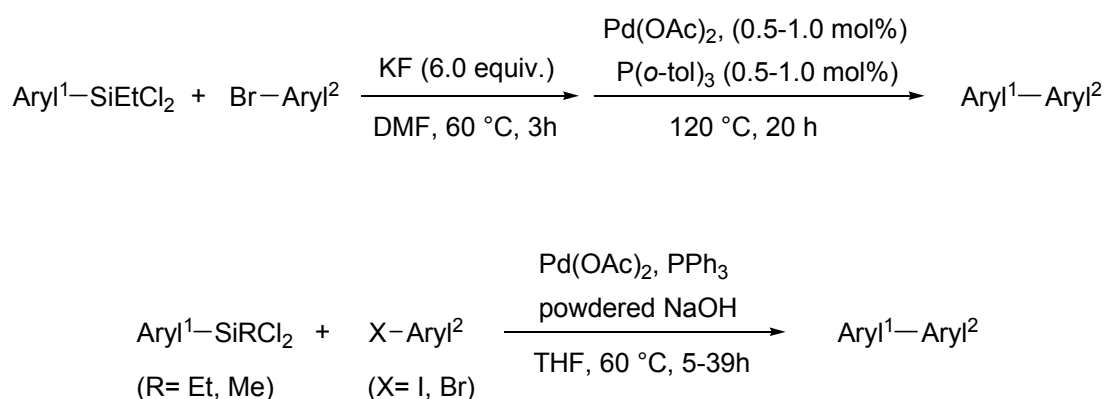
Hiyama⁹ reported a vast improvement in cross-coupling reaction using organosilicon compounds as coupling reagents with fluorosilanes, and the corresponding cross-coupling products were obtained in a good yield using both fluorosilane and fluoride ions. It was also shown to be essential for the cross-coupling of organosilicon compounds to form pentacoordinated silicate in the reaction system (Scheme 5). Hiyama's achievement was a major breakthrough in cross-coupling reactions using

organosilicon, and it is an extremely significant achievement in terms of organic synthesis.



Scheme 5. Cross-coupling reactions of fluorosilanes.

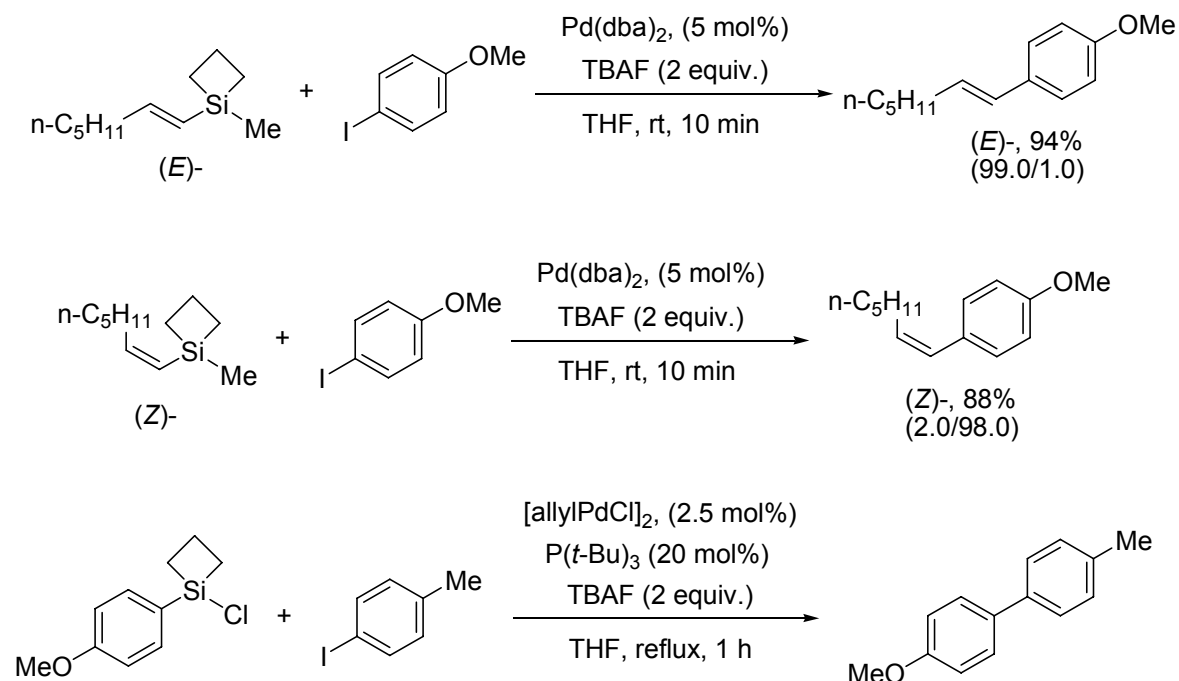
Hityama used chlorosilanes, which are commercially available and in large quantities, as coupling reagents for cross-coupling reactions (Scheme 6).¹⁰ This reaction also requires a fluoride ion as activator in the early stage, however, it was found that powdered sodium hydroxide (NaOH), which is one of the most inexpensive and available inorganic bases, was particularly effective as an activator.¹¹



Scheme 6. Cross-coupling reactions of chlorosilanes.

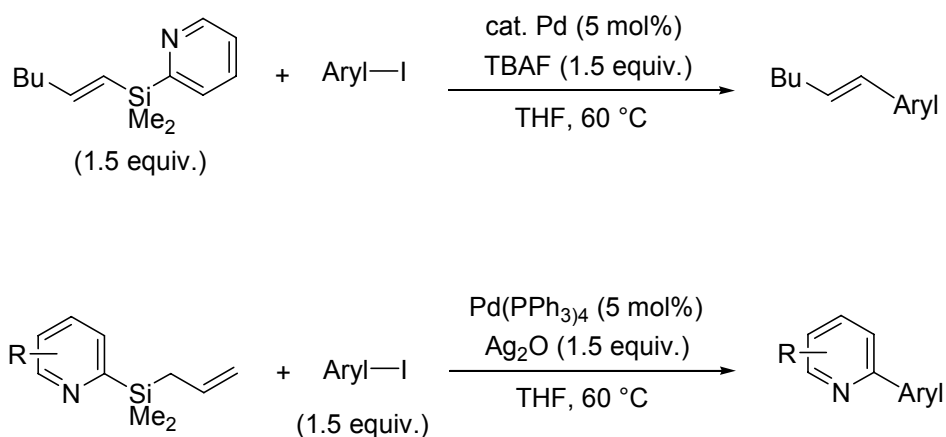
Although chlorosilanes are commercially available compounds and in large quantities, the extreme moisture sensitivity of chlorosilanes requires strict storage and handling. Since hydrochloric acid (HCl), which is generated from the contact of water and chlorosilanes, decomposes storage containers and chemicals, chlorosilanes are far from useful reagents in organic synthesis.

Denmark described alkenyl- or arylsilacyclobutanes, which are four-membered cyclic silane compounds, as effective coupling reagents for cross-coupling reactions.¹² The coupling reactions of alkenylsilacyclobutane were proceeded without phosphine ligands. However, tri(*tert*-butyl)phosphine ($P(tBu)_3$), which is known as a strongly coordinative phosphine ligand, is required in reactions of arylsilacyclobutane because of its lower reactivity.



Scheme 7. Cross-coupling reactions of alkenyl- or arylsilancyclobutane promoted by tetra(*N*-*tert*-butyl)ammonium fluoride (TBAF).

Yoshida reported that alkenyl(2-pyridyl)silanes¹³ react with aryl halides to afford the corresponding alkenyl- or 2-pyridyl-substituted cross-coupled product (Scheme 8). The reactivity is due to the strong coordination effect of the 2-pyridyl group on the silicon atom. In this 2-pyridyl-introducing reaction, a silver(I) oxide (Ag₂O) activator and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) catalyst were particularly effective. We previously found that Ag₂O was effective as an activator for organosilicon-based coupling reaction.¹⁴ The coupling reaction using an Ag₂O activator is described in Section (b) of this Chapter.



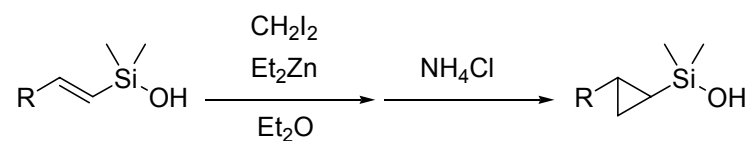
Scheme 8. Cross-coupling reactions of 2-pyridylsilanes.

Organosilicons are known as awkward reagents for organic synthesis since the reactivity for cross-coupling reactions of organosilicons is lower than that of organoborons and organotin. The reactivity for coupling reactions using organosilicons has recently been greatly enhanced by the introduction of substituents on the silicon atom or the addition of fluoride ions. However, organosilicon-based coupling reactions are far from useful since these reactions require sensitive handling and/or the use of less common organosilicon compounds such as fluorosilanes, silacyclobutanes, and 2-pyridyl-substituted-silanes. Therefore, cross-coupling reactions with easily obtainable and stable organosilicon compounds are desirable.

(b) Organic Synthesis Using Organosilanols

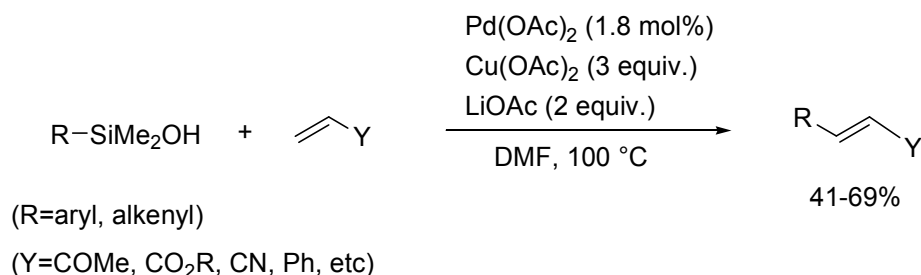
Organosilanols, which have a hydroxy group on the silicon atom, are unexpectedly stable in ambient condition. Silanols are relatively stable enough to handle in ambient conditions unlike chloro- and fluorosilanes. We first focused on organosilanols and found that they are used as organosilicon reagents for organic synthesis.

We reported on the Simmons-Smith cyclopropanation of alkenylsilanols with diethylzinc and diiodomethane to afford the corresponding cyclopropanylsilanols (Scheme 9).¹⁵ Alkenylsilanol served as a synthetic equivalent of allylic alcohol to significantly enhance the rate of cyclopropanation.



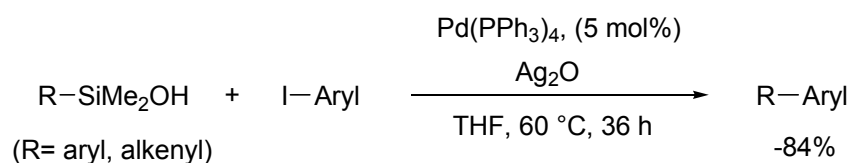
Scheme 9. Simmons-Smith cyclopropanation of alkenylsilanols.

We also reported a Mizoroki-Heck (MH)-type reaction of organosilanols with a terminal olefin in the presence of a stoichiometric amount of palladium acetate ($\text{Pd}(\text{OAc})_2$).¹⁶ Furthermore, we also found that this MH-type reaction proceeded in the presence of 1.8 mol % of $\text{Pd}(\text{OAc})_2$, 3 equiv. of copper acetate ($\text{Cu}(\text{OAc})_2$), and 2 equiv. of lithium acetate (LiOAc) (Scheme 10).¹⁷ This MH-type reaction was the first example of a carbon-carbon bond-forming reaction of organosilanols, and a silicon-carbon (Si-C) bond of an organosilanol, which had not been used in organic synthesis previously, was shown to be practical for organic synthesis.



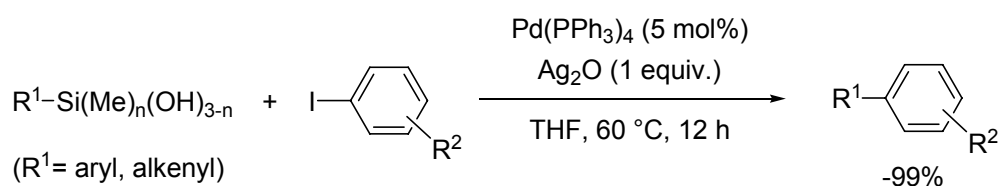
Scheme 10. Palladium-catalyzed Mizoroki-Heck-type reaction of arylsilanols with terminal olefins.

As has been previously described, cross-coupling reactions are general carbon-carbon bond-forming reactions. We reported cross-coupling reactions of arylsilanols with aryl iodides in the presence of a palladium-catalyst (Scheme 11).^{14a} In this reaction, we found silver(I) oxide was effective as a reaction activator. A fluoride ion, which was used as an activator for the cross-coupling reactions of organosilicon compounds, was not effective in this reaction system.



Scheme 11. Cross-coupling reaction of organosilanols with aryl iodides promoted by Ag₂O.

We also found the reactivity of silanediols to be superior to the corresponding silanols (Scheme 12).^{14b} Aryl- and alkenylsilanediols and -triols were easily synthesized from the corresponding chlorosilanes and subjected to similar cross-coupling reactions. The comparison of silanol, silanediol, and silanetriol demonstrates a higher coupling efficiency of silanediol and silanetriol than that of silanol. It should also be pointed out that several coupling reactions were found to proceed smoothly starting from the use of dichloro- or trichloroaryl and -alkenyl silicon reagents via hydrolysis, and the cross-coupling sequence without purifying formed crude silanediol or silanetriol.



Scheme 12. Cross-coupling reactions of silanediols and silanetriols.

The role of silver oxide in this reaction can be explained by two properties (Figure 1). First, the oxygen atom of the Ag_2O serves as a nucleophile to activate the silicon, generating the necessary silicate intermediate. Second, the silver atom promotes halide extraction from the aryl-palladium-iodide intermediate.

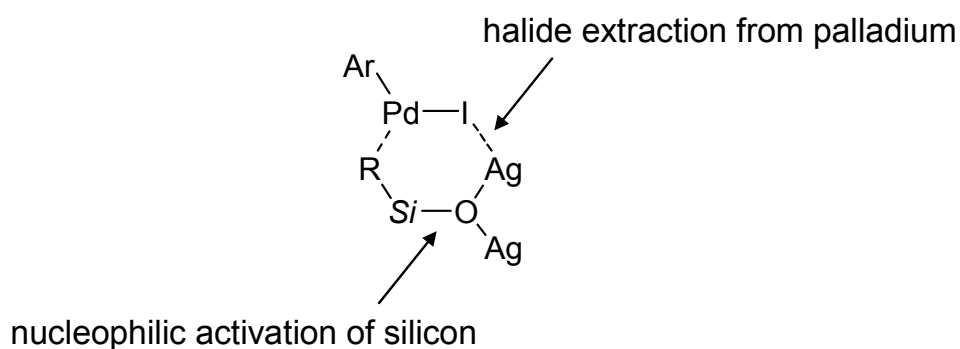
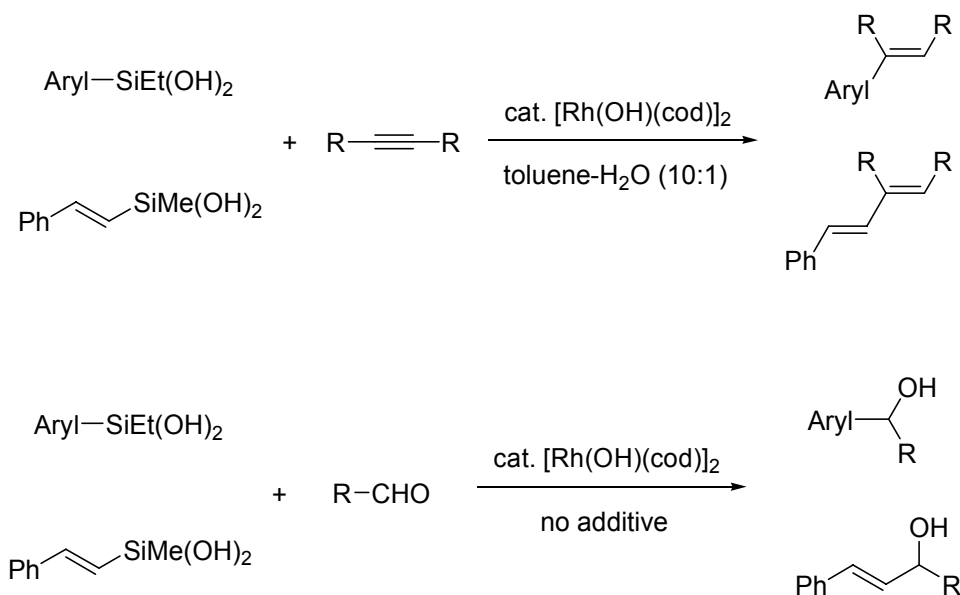


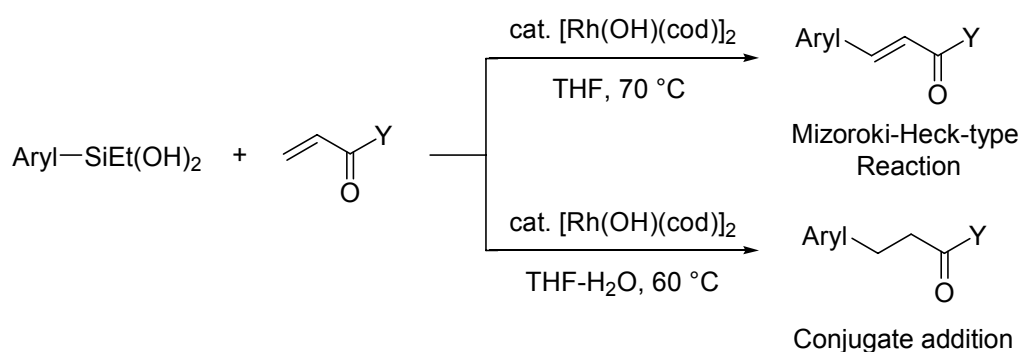
Figure 1. Plausible intermediate of cross-coupling.

Silanediols, which are readily available by hydrolysis of the corresponding chlorosilanes, are particularly useful reagents. We have recently found that rhodium is also a suitable catalyst for the transmetalation of silanediols and can catalyze hydroarylation and α -alkenylation of alkynes with silanediols and addition of aryl- and alkenylsilanediols to aldehydes. The most effective rhodium complex is hydroxorhodium (Scheme 13).¹⁸



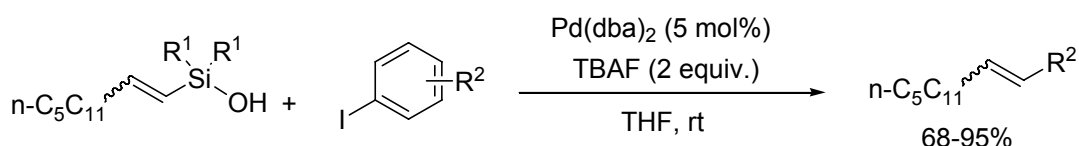
Scheme 13. Hydroxorhodium catalyzed carbon-carbon bond-forming reactions of silanediols with alkynes or aldehydes.

Furthermore, we revealed that the hydroxorhodium-catalyzed MH-type reaction of silanediols underwent smoothly in ethereal solvents such as tetrahydrofuran (THF) and 1,4-dioxane. We also reported that the hydroxorhodium complex can catalyze the addition of such species to α,β -unsaturated carbonyl compounds by the addition of water to the reaction solvent.¹⁹ Interestingly, simply changing the solvent from THF to THF/H₂O gave the 1,4-conjugate addition product (Scheme 14). In other words, the rhodium-catalyzed reaction of silanediols with α,β -unsaturated esters can be directed toward an MH-type reaction and/or conjugate addition.



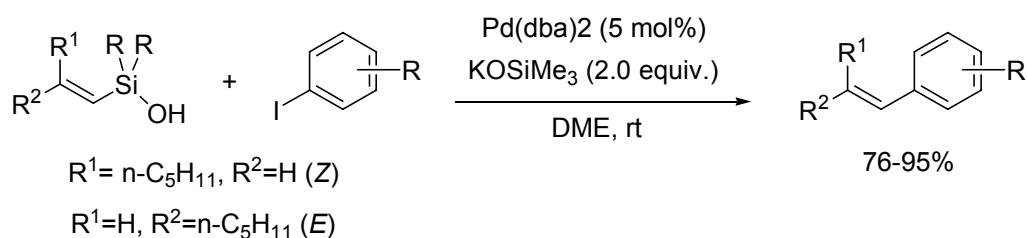
Scheme 14. Hydroxorhodium complex-catalyzed reaction of arylsilanediols with α,β -unsaturated carbonyl compounds; MH-type reaction vs. conjugate addition.

As presented above, we focused on organosilanols and showed that they are powerful reagents for various organic reactions. The driving force of these reactions is attributed to the hydroxy group on the silicon atom. After we reported cross-coupling reaction of organosilanols with aryl iodides, Denmark also reported a coupling reaction of silanol, which is similar to our report. The coupling reaction was performed using alkenylsilanol with aryl iodides in the presence of TBAF or tetrabutylammonium hydroxide (TBAOH) as an activator. Although the reaction proceeded within 10 min, the reagent was limited in alkenylsilanols. (Scheme 15).²⁰



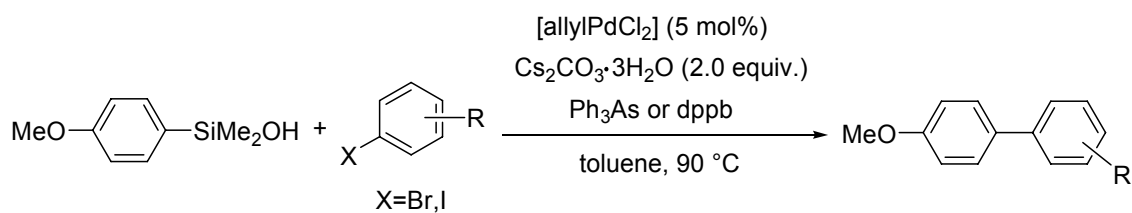
Scheme 15. Cross-coupling reactions of alkenylsilanols promoted by TBAF.

We have studied the reactivity for cross-coupling reactions of alkenyl- and arylsilanols by the coupling of silanols with aryl iodides using Ag_2O as an activator and showed that the reactivity of alkenylsilanols was much higher than that of arylsilanols. Denmark also studied the non-fluoride reaction system of alkenylsilanols and reported KOSiMe_3 ²¹ was an effective activator (Scheme 16).



Scheme 16. Cross-coupling reactions of alkenylsilanols with aryl iodides promoted by KOSiMe_3 .

In addition, Denmark recently reported that Cs_2CO_3 ²² was also effective for the cross-coupling of arylsilanols (Scheme 17), however, this reaction is not a useful method since organic arsenes, which are known as an extremely toxic material, are required as a ligand.



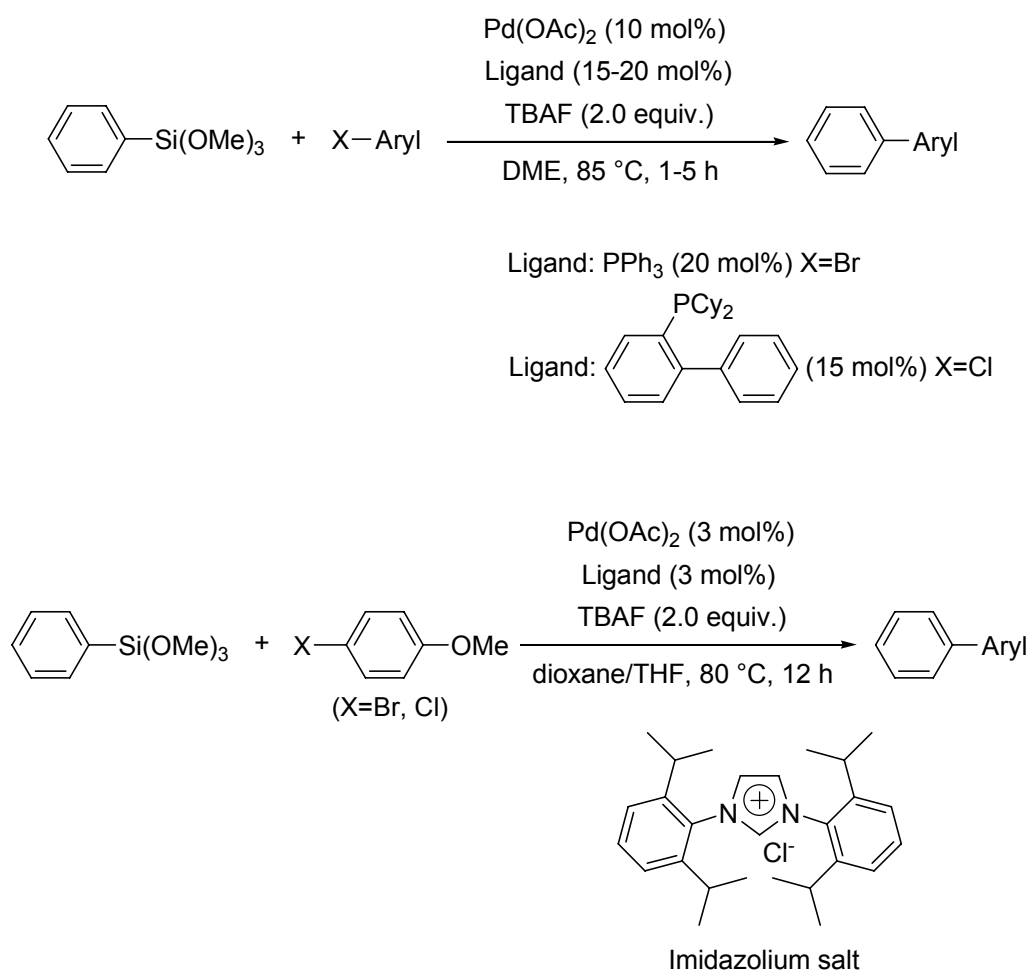
Scheme 17. Cross-coupling reactions of arylsilanols with aryl halides promoted by Cs_2CO_3 .

As has already been mentioned, organosilanols are extremely important reagents for carbon-carbon bond-forming reactions. We first focused on the importance and reactivity of organosilanols and developed a new class of carbon-carbon bond-forming reactions. The reactivity of organosilanols for organic synthesis depends on the presence of the silicon-oxygen bond.

(c) Organic Synthesis of Organosilicon Compounds Bearing Si-O Bonds

As presented above, we first focused on the importance of organosilanols as reaction reagents and developed various reactions. The driving force of these reactions is attributed to the hydroxy group on the silicon atom. That is to say, since the reactivity of organosilicon compounds is closely associated with the silicon-oxygen (Si-O) bond, particular attention was paid to the organosilicon compounds bearing silicon-oxygen (Si-O) bonds.

DeShong found that aryltrialkoxysilane²³ reacts with several aryl halides in the presence of Pd(OAc)₂/PPh₃. The cross-coupling of arylsilyl ethers with aryl chlorides has also been possible when a different ligand, 2-(dicyclohexylphosphine)biphenyl, which is known to activate the palladium-catalyst in other palladium-catalyzed coupling reactions with aryl chlorides, was used as a phosphine ligand. However, this reaction requires higher loading of the palladium catalyst (10 mol%) and phosphine ligand (15-20 mol%) and is not convenient. Soon after DeShong's report, Nolan also reported an effective system consisting of Pd(OAc)₂ and an imidazolium ligand (Scheme 18).²⁴

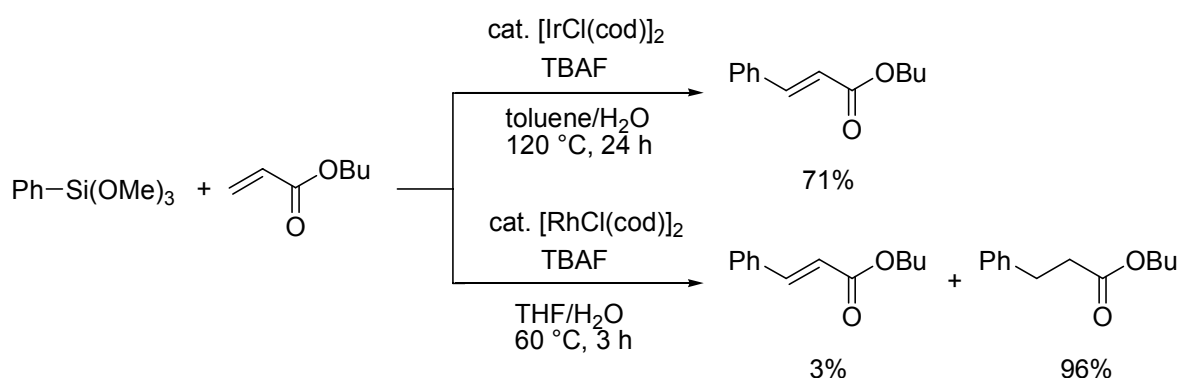


Scheme 18. Cross-coupling reactions of aryltrimethoxysilanes with aryl halides promoted by TBAF.

While trialkoxysilanes have three Si-OR bonds, organosilanols have one Si-OH bond. In other words, a hydroxy group on the silicon atom has high reactivity to promote the cross-coupling reaction.

We also studied the reaction of PhSi(OMe)_3 as an organosilicon reagent. We revealed that an iridium catalyst is effective for the MH-type addition/elimination reaction of α,β -unsaturated carbonyl compounds with several organosilicon reagents.²⁵ The

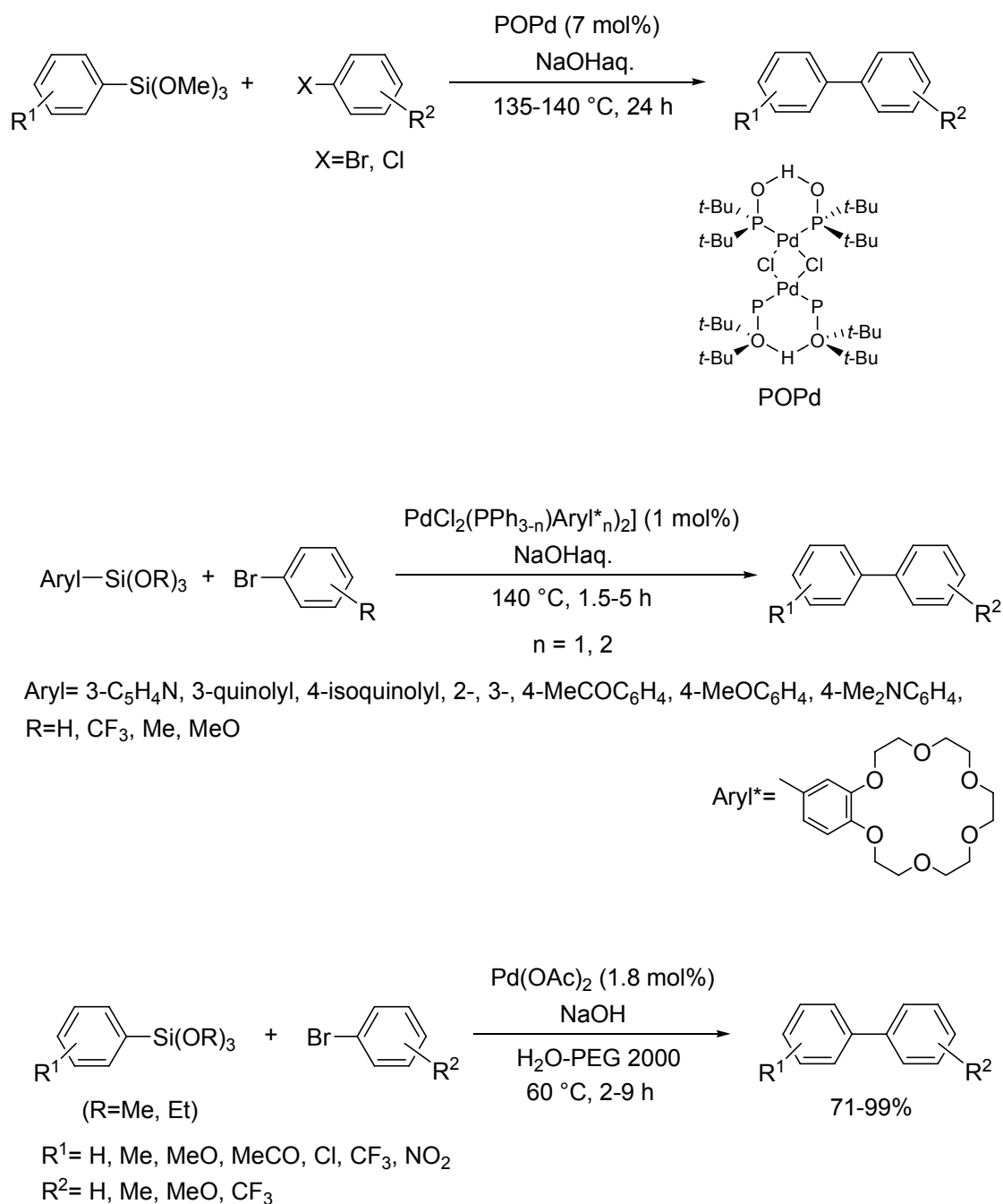
reaction of $\text{PhSi}(\text{OMe})_3$ with butyl acrylate in the presence of 5 mol % of $[\text{IrCl}(\text{cod})]_2$ and TBAF in toluene/ H_2O (6/1) at 120 °C for 24 h afforded the addition/elimination product in a 71% yield, while a conjugate addition product was not obtained. This result is in sharp contrast to that of a related reaction with the rhodium catalyst $[\text{RhCl}(\text{cod})]_2$ at 60 °C in THF/ H_2O (6/1)¹⁹, which affords the conjugate adduct as the major product with high selectivity (Scheme 19).



Scheme 19. Iridium- or rhodium-catalyzed MH-type reactions of $\text{PhSi}(\text{OMe})_3$ with butyl acrylate promoted by TBAF.

In addition, fluoride-free cross-coupling reactions of aryltrialkoxysilane with aryl halides in an aqueous medium have recently been developed (Scheme 20). Wolf reported the cross-coupling reaction of aryltrimethoxysilane with aryl halides in water promoted by NaOH using a palladium-phosphinous acid complex $[\{(\text{tBu})_2\text{P}(\text{OH})-(\text{tBu})_2\text{PO}\}\text{PdCl}]_2$.²⁶ Jesús reported the palladium-crown-ether complex catalyzes the cross-coupling of arylsiloxanes with aryl bromides.²⁷ These reactions are

performed using a water-soluble palladium catalyst, In contrast, Zhang has recently reported that $\text{Pd}(\text{OAc})_2$, which is a common palladium-catalyst, catalyzed fluoride-free cross-coupling of aryltrimethoxysilane with aryl bromides in an aqueous medium. The reaction uses poly(ethylene glycol) (PEG)²⁸ as a reaction media. This $\text{Pd}(\text{OAc})_2$ -based reaction is remarkably effective since this reaction is proceeded by the addition of commercially available PEG and does not required a special palladium catalyst such as a water-soluble catalyst.



Scheme 20. Fluoride-free cross-coupling reactions of aryltrialkoxysilanes promoted by NaOH in aqueous medium.

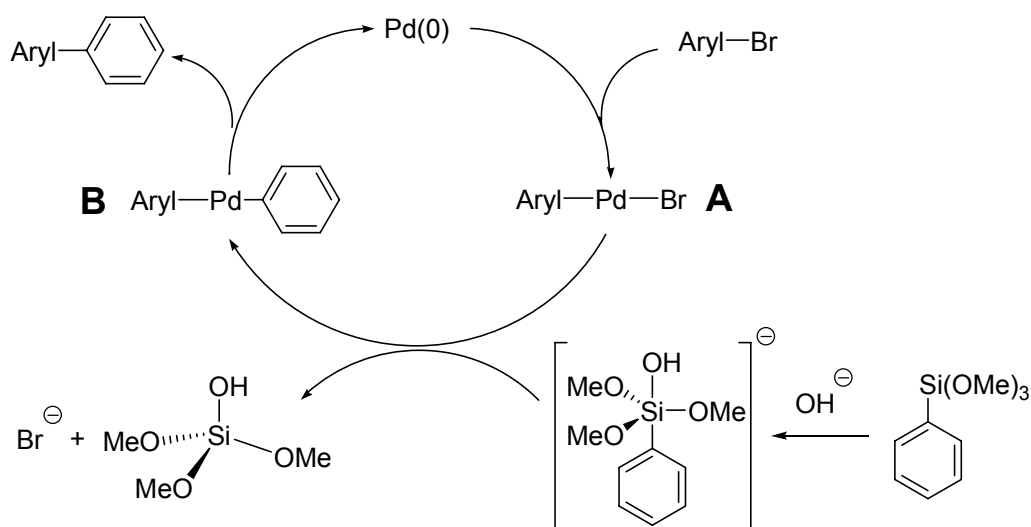
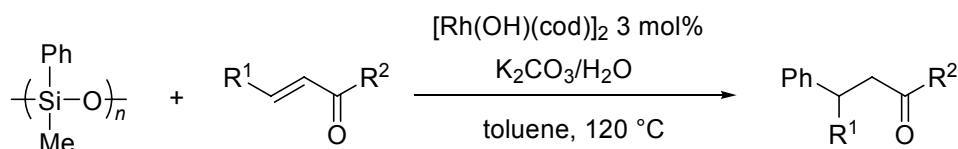


Figure 2. Wolf and Zhang's catalytic cycle of NaOH-promoted palladium-catalyzed cross-coupling reaction of aryltrimethoxysilane.

Wolf and Zhang also proposed the reaction mechanism of the NaOH-promoted cross-coupling reaction of aryltrimethoxysilane (Figure 2). The initial oxidative addition of aryl bromide to $\text{Pd}(0)$ generates arylpalladium intermediate **A**, which reacts with the pentavalent silicate formed in situ in sodium hydroxide solution to afford (aryl)-palladium(II)-(aryl) species **B**. The subsequent reductive elimination affords the biaryl product with the regeneration of active $\text{Pd}(0)$ to complete the catalytic cycle.

On the other hand, the thermal and chemical stability of silicone has led to the wide use of silicone, rubber, grease, and oil. We revealed that the reaction of poly(methylphenylsiloxane), which is industrially used as highly thermo-resistant silicone oil, with α,β -unsaturated carbonyl compounds in the presence of aqueous

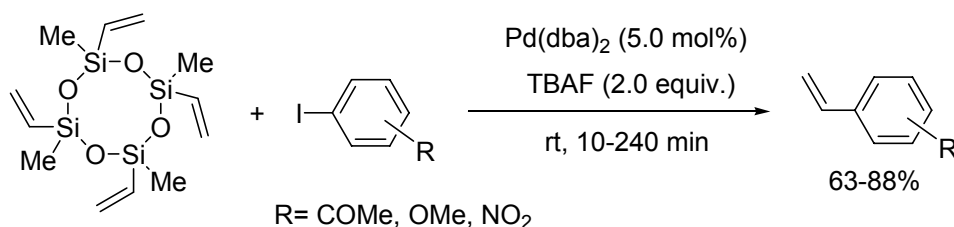
K_2CO_3 and a catalytic amount of $[\text{Rh}(\text{OH})(\text{cod})]_2$ gives the 1,4-conjugate addition product. (Scheme 21).²⁹



Scheme 21. Rhodium catalyzed conjugate addition of silicone to α,β -unsaturated carbonyl compounds

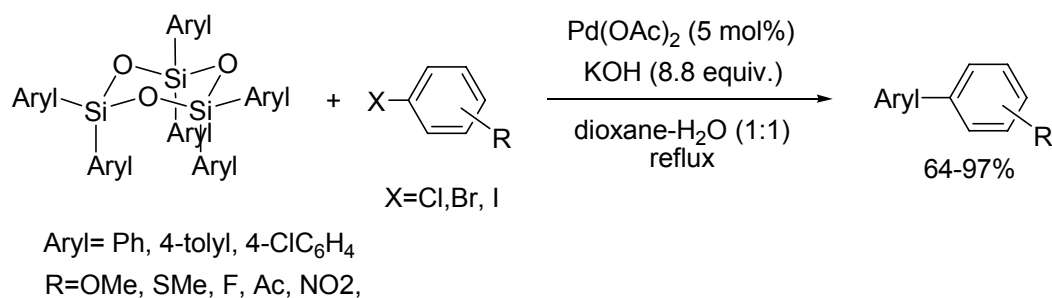
Proceeding to our studies on the conjugate addition, we have shown that cross-coupling of polysiloxanes or cyclic siloxanes occurs with organic halides in the presence of a palladium catalyst, which is a part of this Thesis.

Soon after our report, a cross-coupling reaction using cyclic vinylsiloxanes³⁰ as a coupling reagent was also reported by Denmark (Scheme 22).



Scheme 22. Vinylation of aryl iodides with commercially available cyclic siloxane.

Fugami also found that hexaarylcyclotrisiloxane, which is one of the most stable derivatives of diarylsilanediol, undergoes a palladium-catalyzed cross-coupling reaction with aryl halides (Scheme 23).³¹ This reaction is performed in an aqueous medium taking potassium hydroxide as an activator.



Scheme 23. Cross-coupling reaction of hexaarylcyclotrisiloxane with aryl halides Promoted by KOH.

As summarized in this section, studies on organosilicon compounds as coupling reagents have been rapidly increasing. Organosilane compounds may be a new class of viable and useful coupling reagents because of their low cost, low toxicity, and high chemical stability. Since there is a large amount of silicon sources on earth, a continuous supply of silicon compounds is guaranteed. The cross-coupling reactions of organosilicon compounds are expected to enable large contributions in such fields as, medicine, environmental protection, agriculture, chemical engineering, and pharmaceuticals.

3) Organic Polymers for Rechargeable Batteries

Lithium-ion rechargeable batteries are widely used in portable electronic devices such as cellular phones and laptop computers. However, lithium-ion rechargeable batteries have the largest energy density, and LiCoO₂ as a cathode-active material in these batteries is expensive, toxic, and present thermal safety problems.³² Organic materials, rather than transition-metal oxides, as cathode active material make rechargeable batteries more environmentally friendly.³³

The first organic-based charge storage device was a rechargeable battery using a conducting polymer as an active material. A number of conducting polymers³⁴ were synthesized and have recently been studied as material for not only rechargeable batteries but also photovoltaic devices.³⁵ In particular, the electrochemical properties of conducting polymers as organic semiconductors for light emitting diodes (OLEDs) and organic thin-film solar cells have been intensively studied. The chemical structures of typical conducting polymers are shown in Figure 3.³⁶

Energy density is one of the most significant points for rechargeable batteries. Although rechargeable batteries using polyacene, which is a typical conducting polymer used as an active material, is in practical use, conducting polymer-based rechargeable batteries³⁷ is not yet been widely available because of their low energy density. The reason for the low energy density can be explained by the low degree of doping concentration of conducting polymers. Since the doped electrons within the polymer chain are highly delocalized, the large interaction between charged electrons, which is called Coulomb repulsion, arises. Therefore, it is difficult for conducting polymer-based

batteries to increase the energy density. The electrode reaction of a conducting polymer-based rechargeable battery is shown in Scheme 24.³⁶

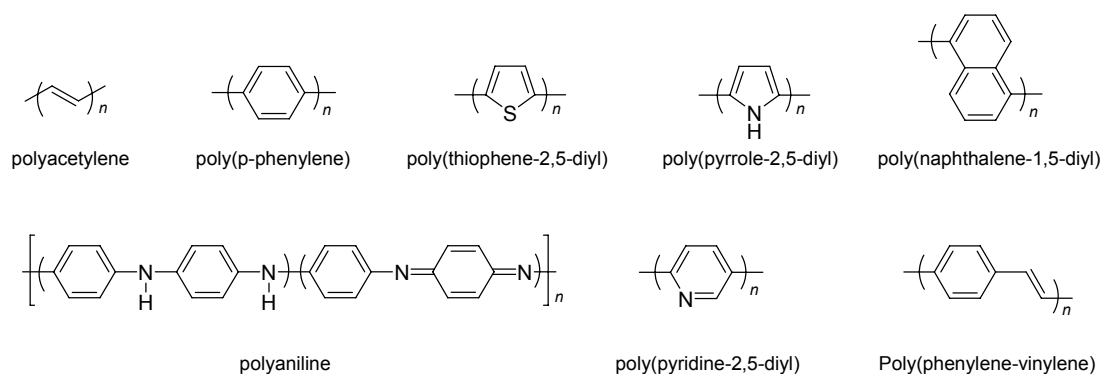
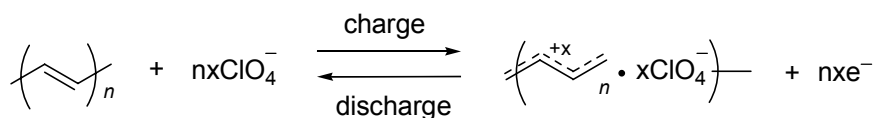
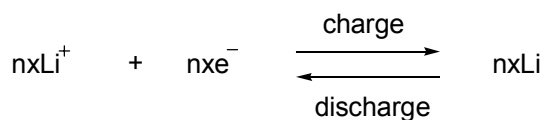


Figure 3. Chemical structures of typical conducting polymers.

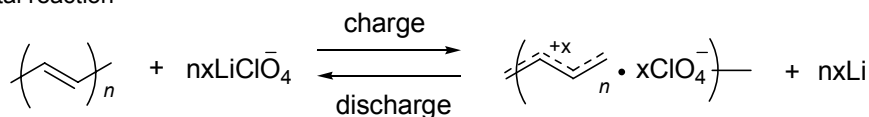
Cathode reaction



Anode reaction



Total reaction



Scheme 24. Electrode reaction of rechargeable battery using polyacetylene.

Visco reported a new class of organic battery, which uses disulfide compounds³⁸ as the cathode active material (Figure 4). This battery uses the bonding and dissociation

state of the S-S bond (Scheme 25). These batteries with disulfide compounds had extremely large theoretical capacity and were expected to have high capacity. Although a large capacity was obtained initially, the capacity decreased after a few charge-discharge cycles. Furthermore, there was a significant problem in that the charge-discharge speed was extremely slow. The disulfide batteries have not been put into practical use because of their insufficient charge-discharge cycles and speed.

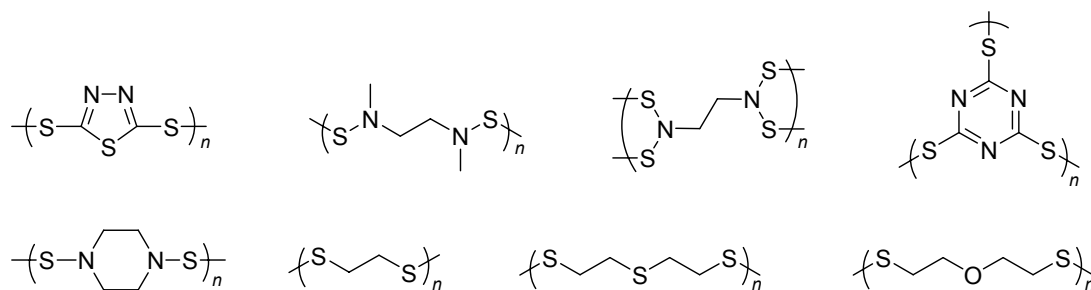
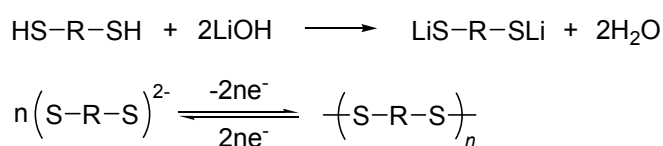


Figure 4. Chemical structures of organosulfur redox polymers.



Scheme 25. Reaction mechanism of polydisulfide battery system.

Therefore, we explored organic radical polymers as cathode active materials for lithium-ion batteries, which are called “organic radical batteries (ORBs)”.³⁹ We

synthesized a stable radical polymer, poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (PTMA). This polymer contains 2,2,6,6-tetramethylpiperidiny-*N*-oxy (TEMPO) radical moiety, which is chemically robust as well as rapidly, reversibly, and nearly stoichiometrically oxidized to the corresponding oxoammonium cation (Figure 5).

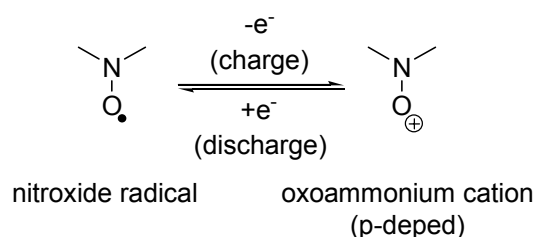
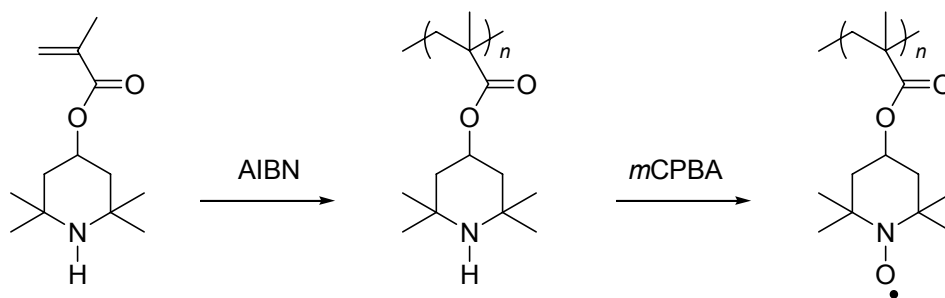


Figure 5. Electrochemical redox process of nitroxide radicals.

We developed a rechargeable battery with organic radical polymer PTMA as the cathode active material. The first report of an ORB showed an average discharge voltage of 3.5 V and a discharge capacity of $77 \text{ mAh} \cdot \text{g}^{-1}$, which corresponds to 70% of its theoretical value. The ORB is expected to be a quick-charging and high-power discharge-type battery since the electron-transfer rate constant k_0 for the nitroxide radical is estimated using the Nicholson method to be approximately $10^{-1} \text{ cm} \cdot \text{s}^{-1}$, which places the nitroxide radical in the category of a rapid electron-transfer system.⁴⁰ We also described the high-power properties of Al-laminate-shaped cells containing PTMA.⁴¹

Meanwhile, PTMA was synthesized by radical polymerization using a methacrylate monomer bearing an amino group and successive oxidation of an amino group of the

polymer. However, this indirect synthetic method was accompanied by incomplete oxidation of an amino group into a nitroxyl radical, resulting in insufficient radical concentration as charge-storage material (Scheme 26).

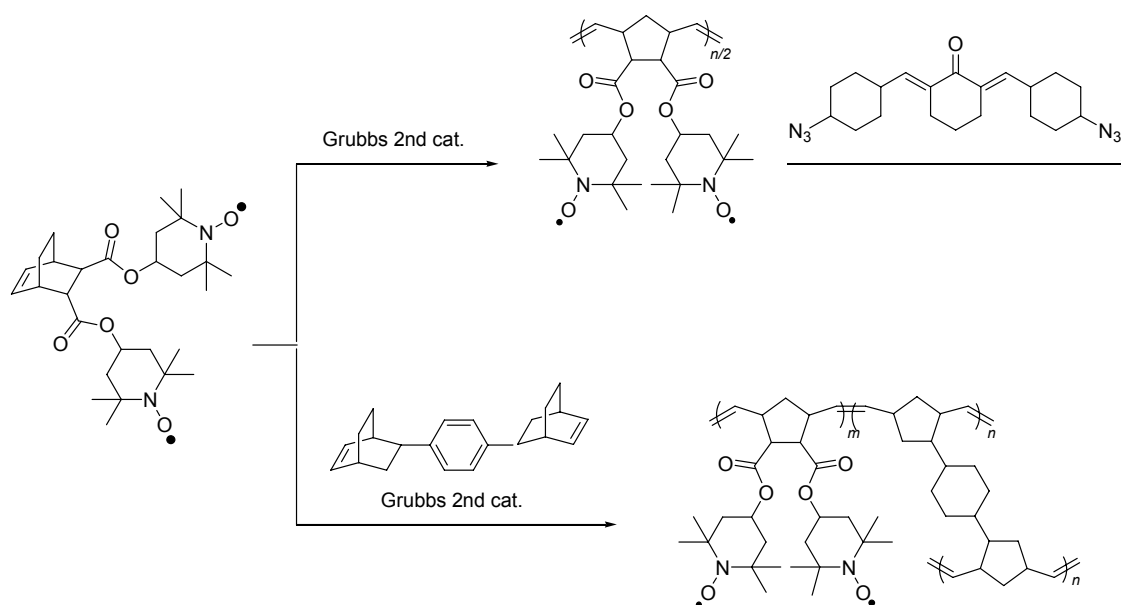


Scheme 26. Synthetic route of TEMPO-substituted polymethacrylate (PTMA).

Nishide and Masuda independently reported a direct synthetic method and battery properties of polynorbornene bearing a TEMPO radical moiety (Scheme 27).⁴² The TEMPO-containing norbornene and 7-oxanorbornene monomers were synthesized and polymerized via ring-opening metathesis using a ruthenium-carbene catalyst, which is referred to as “Grubbs 2nd generation” (Figure 6). The ruthenium-catalyzed polymerization of monomers afforded corresponding polymers in a good yield since the TEMPO moiety did not inhibit polymerization.

Nishide also succeeded in forming radical polymer film on an indium tin oxide (ITO)/glass substrate by photocrosslinking of polynorbornene bearing a TEMPO radical moiety.^{42a} We have been using carbon as a conducting material for ORBs. In contrast, Nishide observed the reversible redox of the radical polymer thin film, which was formed on the ITO/glass substrate. In other words, electron transfer from ITO to an

organic radical polymer occurred without carbon. It is interesting to note that an ITO/glass substrate can be used as a new collector electrode for organic radical batteries.



Scheme 27. Synthesis of cross-linking TEMPO-substituted polynorbornens.

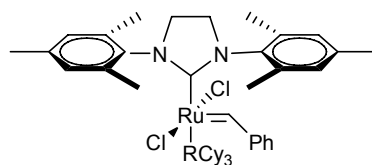
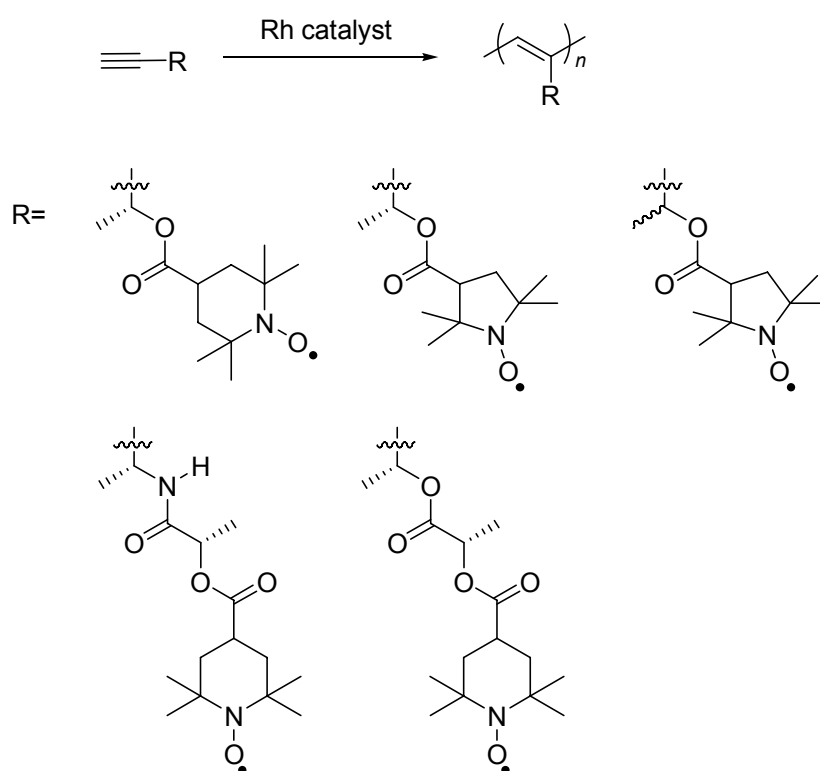


Figure 6. Chemical structure of Grubbs 2nd generation catalyst.

Masuda reported helical acetylene monomers bearing a TEMPO or 2,2,5,5-tetramethylpyrrolidine-*N*-oxy (PROXYL) radical moiety and polymerized them with a rhodium-based transition metal catalyst (Scheme 28).⁴³ The polymerization of acetylenic monomers was carried out using $(\text{nbd})\text{Rh}^+[\eta^6\text{-C}_6\text{H}_5\text{B}(\text{C}_6\text{H}_5)_3]$ or

$[(\text{nbd})\text{RhCl}]\text{-Et}_3\text{N}$ as a catalyst. All of the radical-containing polymers displayed reversible charge/discharge processes, whose capacities were in the range of 43-112 $\text{mAh}\cdot\text{g}^{-1}$. Although several polyacetylene-based radical polymers were proposed by Masuda, the capacities of the polyacetylenes are still lower than that of PTMA (111 $\text{mAh}\cdot\text{g}^{-1}$).



Scheme 28. Chemical structures of helical polyacetylenes bearing TEMPO radical or PROXYL radical.

Masuda also proposed that DNA complexes containing TEMPO radical moiety, which can be considered a new class of cathode-active material (Figure 7).⁴⁴ Although it may

interesting to use DNA structures as active material for rechargeable batteries, the actual capacity is lower than that of PTMA and are far from practical.

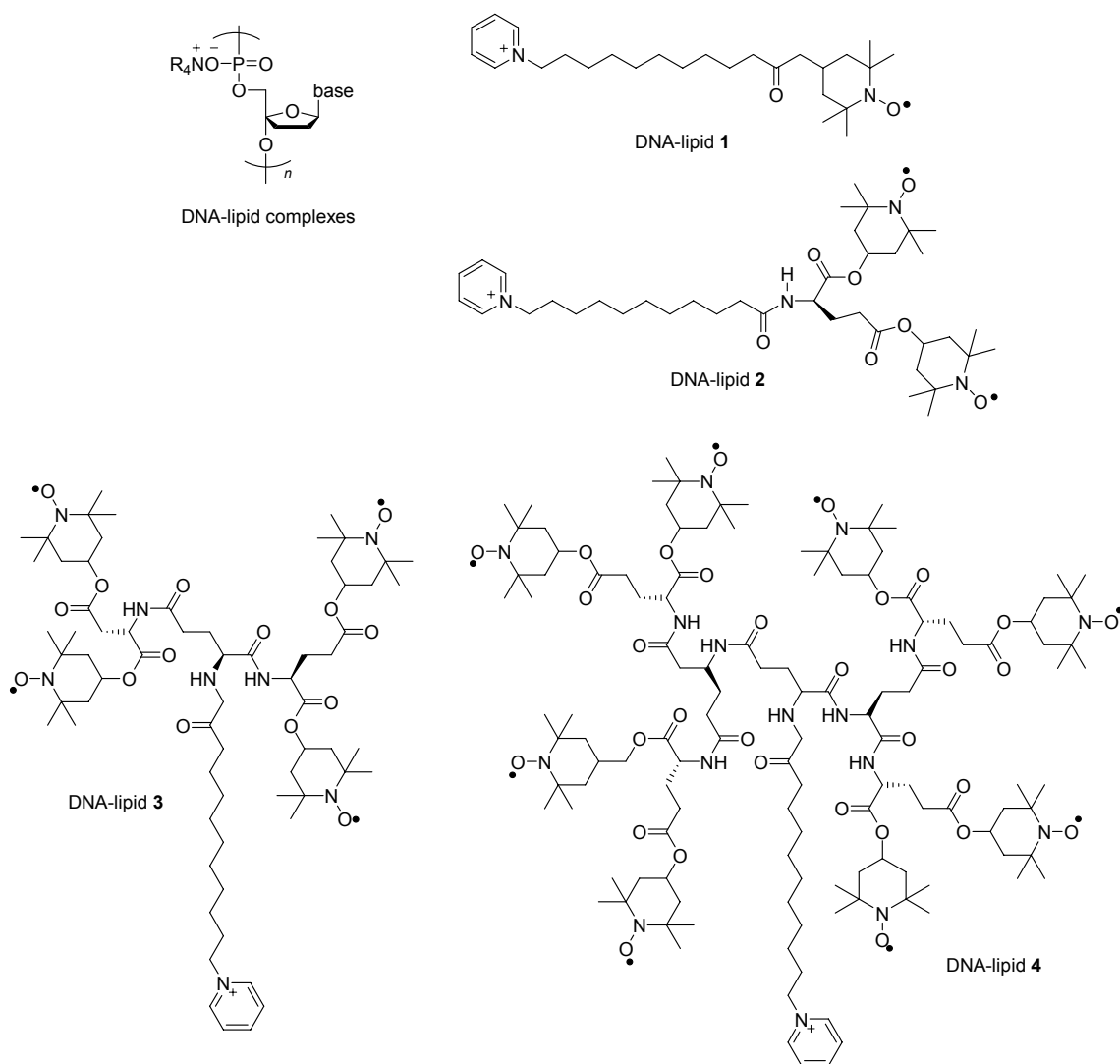


Figure 7. Chemical structures of cationic DNA-lipid carrying TEMPO radicals.

Although a number of TEMPO-containing polymers were synthesized as cathode-active material for ORBs, there are no polymers that exceed the capacity of PTMA. Synthesis of a new class redox-active polymer for ORBs is significant; however,

practicality studies are also required to enable wide use of ORBs. Since the battery capacity significantly depends on the amount of active materials in the electrode, far more polymer-rich electrodes are necessary.

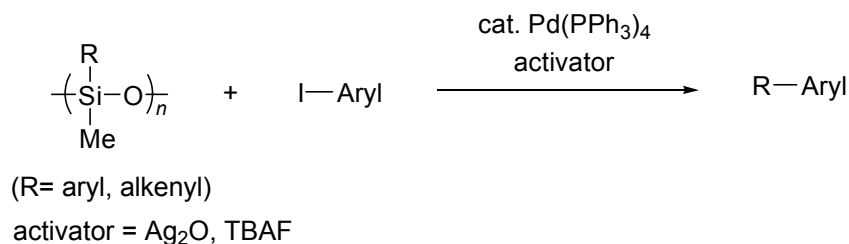
4) Purpose and Scope

Transition-metal-catalyzed coupling reaction is extensively used in syntheses of pharmaceutical products, agricultural chemicals, and electronic materials. Although organoboron and organotin compounds are used as reagents for carbon-carbon bond-forming reactions, these compounds are expensive, toxic, and present safety problems. As summarized in this Chapter, organosilicon compounds have been studied as carbon-carbon bond forming reagents via cross-coupling. Consequently, the Author focused his attention on the coupling reaction using organosilicon compounds as next-generation coupling reagents because of their low cost, low toxicity, and high availability.

On the other hand, polysiloxanes (silicone) have not been recognized as organosilicon reagents for such transition-metal-catalyzed coupling reactions. The use of poly(organosiloxane) as a source of a pseudo organometallic reagent in carbon-carbon bond-forming reactions can be considered a new class of organosilicon reagent for organic synthesis.

Chapter 1 describes that poly(methylphenylsiloxane), which is a commercially available silicone oil with a high thermal stability, is practical as an organosilicon reagent for palladium-catalyzed cross-coupling reactions with organic electrophiles (Scheme 28). The Author describes the scope and limitation of the coupling reaction of silicone bearing aryl and alkenyl groups in an organic moiety of the silicon substituent.

Chapter 1



Scheme 28. Cross-coupling reaction of silicone with aryl halide

Lithium-ion rechargeable batteries are widely used in portable electronic devices such as cellular phones and laptop computers; however, LiCoO₂ as a cathode active material in these batteries is expensive, toxic, and presents thermal safety problems. Organic materials, rather than transition metal oxides, as cathode active material for rechargeable batteries make them more environmentally friendly. Since long-term stability is required for rechargeable batteries, high-chemical and -thermal resistant silicone is available as active material for rechargeable batteries. In Chapter 2, the Author studied silicone as an electrode-active material for rechargeable batteries. Silicone-based radical polymers were obtained by transition-metal-catalyzed reactions of poly(hydromethylsiloxane) (PMHS) with TEMPO derivatives (Figure 8).

Chapter 2

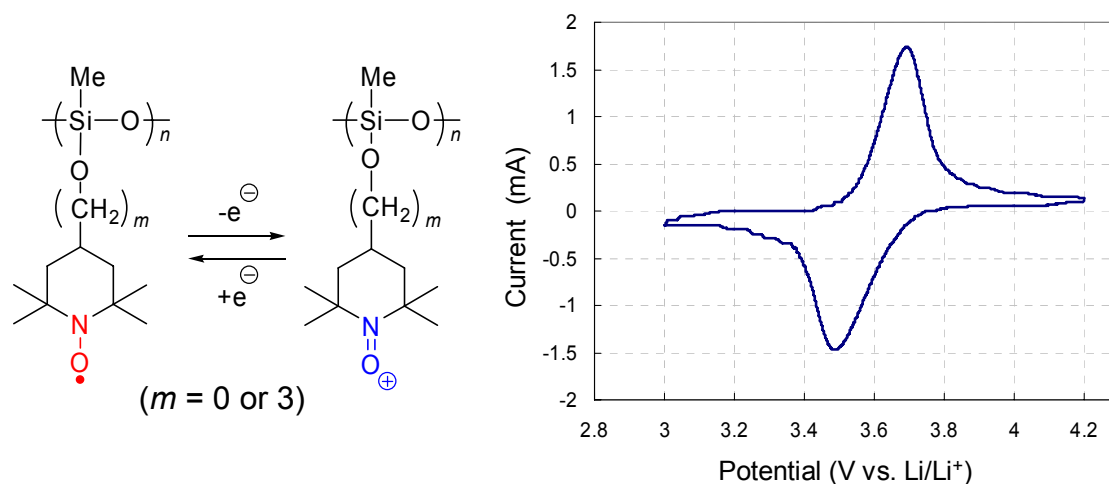
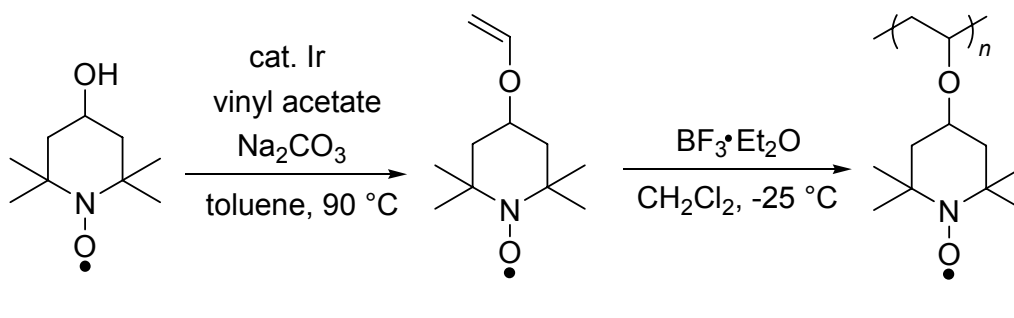


Figure 8. Chemical structure of silicon-based radical polymer and corresponding cyclic voltammogram.

The battery capacity depends on the radical density of radical polymers. Poly(vinyl ether) is one of the simplest structures of all general-purpose polymers. The simple structure of poly(vinyl ether) produces a much higher capacity than that of polymethacrylate or polysiloxane. Although the chemical structure of vinyl ether is simpler than that of methacrylate (PTMA), the synthetic methods of vinyl ethers are not plausible due to their severe reaction conditions or the toxicity of the mercury compounds. The Author focused on the iridium-catalyzed transformation of vinyl acetate into vinyl ethers and thereby synthesized vinyl ether bearing a TEMPO radical moiety. Chapter 3 describes a synthetic method of vinyl ether monomer bearing a TEMPO radical moiety and the corresponding radical polymer (PTVE). Furthermore, a

coin-shaped battery with a PTVE/VGCF composite electrode was also fabricated (Scheme 29).

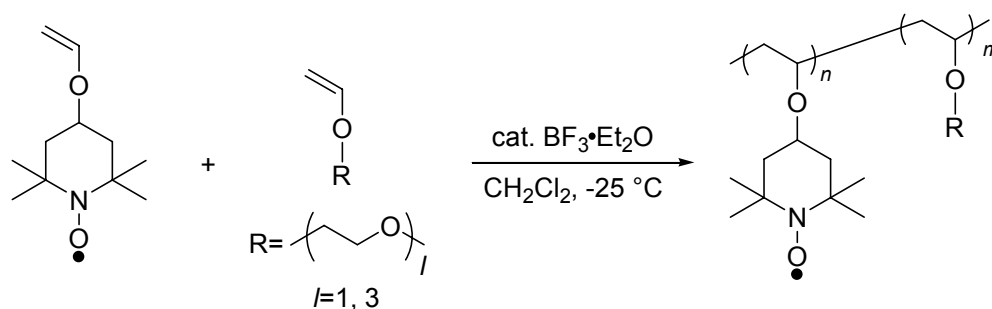
Chapter 3



Scheme 29. Synthesis of vinyl ether monomer bearing TEMPO radical moiety and corresponding polymer (PTVE).

Chapter 4 describes the high-rate discharge properties of organic radical batteries. A copolymerized PTVE was synthesized by cationic polymerization of a vinyl monomer bearing a TEMPO radical and an ethylene oxide or tri(ethylene oxide) (Scheme 30). The charge/discharge properties of copolymerized PTVE improved with the length of the ethylene oxide chain, and high-rate discharge properties of the PTVE synthesized by copolymerization with tri(ethylene oxide) were much better than those of the PTVE homopolymer.

Chapter 4



Scheme 30. Synthesis of PTVE-(ethylene oxide) copolymers

The battery capacity significantly depends on the amount of active materials in the electrode. In Chapter 5, the Author described the fabrication of a practical and polymer-rich organic radical polymer electrode to improve both the battery capacity and the high-rate discharge property. The Author fabricated a high-capacity PTVE/VGCF composite electrode and obtained a radical polymer 80 wt% electrode. The measured capacity of a cell made with this electrode is the highest ever reported for a battery with an all-organic-radical cathode. The Author's aim is to develop an ORB with both high-capacity and high-charge/discharge rates.

Chapter 5

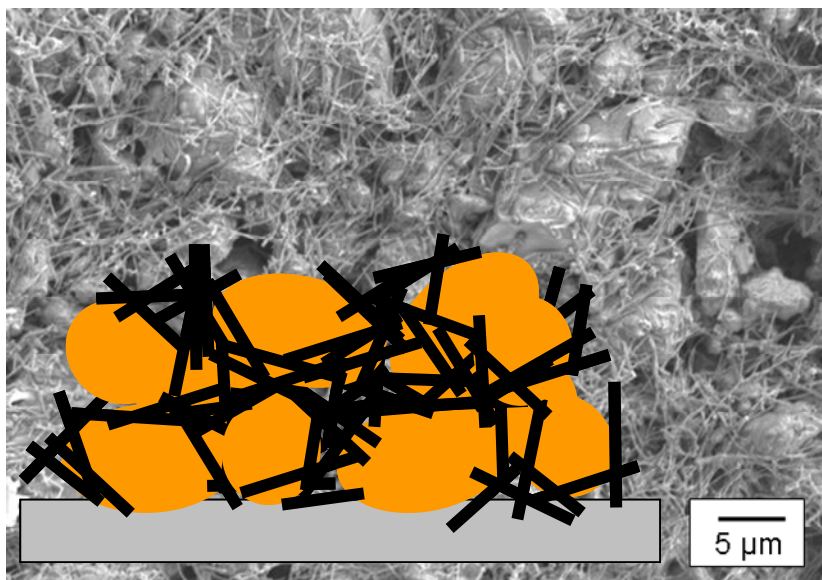


Figure 9. SEM image of PTVE/VGCF composite electrode containing 80 wt.-% PTVE and 15 wt.-% VGCF.

5) References and Notes

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Chapter 1

Silicone as an Organosilicon Reagent for the Palladium-Catalyzed Cross-Coupling Reaction

Abstract: Silicone, poly(diorganosiloxane), serves as an organosilicon reagent for palladium-catalyzed cross-coupling reactions. Treatment of poly[(aryl)methylsiloxane], poly[(alkenyl)methylsiloxane], or cyclic oligosiloxanes with various aryl iodides in the presence of silver(I) oxide (Ag_2O) or tetrabutylammonium fluoride (TBAF) and a catalytic amount of palladium affords the corresponding cross-coupling product in a good to excellent yield. The reaction of silicone with aryl chlorides in the presence of $\text{K}_2\text{CO}_3/\text{H}_2\text{O}$ as an activator proceeded to afford biaryl derivatives in moderate to excellent yields. A wide range of aryl chlorides bearing an electron-donating or electron-withdrawing substituent on the aromatic ring are tolerated.

1.1 Introduction

Silicone has been widely utilized as materials with unique characteristics caused by the strength and flexibility of the Si-O bond. The thermal and chemical stability of the siloxane bond has led to the wide applicability as silicone rubber, grease, and oil. Silicone and its copolymer bearing a functional group on the organic substituent of the silicon atom also serve as various specialty polymers.¹ A number of silicone compounds with various organic substituents are now readily available in silicone industry.

On the other hand, organosilicon compounds have been demonstrated to be valuable carbon-carbon bond forming reagents in organic synthesis.² Several types of organosilanes such as fluoro, chloro, alkoxy, hydroxy, and alkylsilanes react as an organometallic reagent with organic electrophiles in palladium-catalyzed cross-coupling reactions.³ Nevertheless, polysiloxanes (silicone) have not been recognized as an organosilicon reagent for such transition metal-catalyzed coupling reactions so far. Accordingly, the use of poly(organosiloxane) as a source of the pseudo organometallic reagent in carbon-carbon bond-forming reaction can be a novel application of silicone materials in organic synthesis.

We have demonstrated that poly(methylphenylsiloxane), which is a commercially available silicone oil with a high thermal stability, is available as an organosilicon reagent for the palladium-catalyzed cross-coupling reaction with organic electrophiles⁴. Herein, we describe scope and limitation of the coupling reaction of silicone using a variety of poly(organosiloxane)s and cyclic siloxanes bearing aryl and alkenyl groups in an organic moiety of the silicon substituent.

1.2 Experimental

1.2.1 Materials and instruments

Following are applicable to the all experimental parts of this Thesis. All reactions were carried out under an argon atmosphere. Cross-coupling reactions were carried out with standard Schlenk technique. THF, 1,4-dioxane, NMP, and toluene were distilled from sodium/benzophenone. D_3^{Ph} , and D_4^{Ph} were kindly donated by Shin-Ethu Chemical Co. Ltd. Poly(methylphenylsiloxane) was donated by Chisso Chemicals Co. Ltd ($M_w = 2500-2700$). PMHS was purchased from Aldrich Chemicals Co. Ltd. The average degree of polymerization of PMHS was estimated to be approximately 45-50 by ^1H NMR analysis. Silver(I) oxide (Ag_2O) was purchased from Wako Pure Chemical Inc. and used without further purification. TBAF (1 M THF solution) was purchased from Aldrich Chemicals Co. Ltd. NMR spectra were measured on a Varian Mercury 300 spectrometer with $CDCl_3$ as a solvent at ambient temperature. The chemical shifts were recorded in parts per million downfield from tetramethylsilane ($\delta = 0$ ppm) or based on residual $CHCl_3$ ($\delta = 7.26$ ppm) as an internal standard. ^{13}C NMR spectra were recorded at 75.5 MHz with $CDCl_3$ as a solvent with the central line of the solvent ($\delta = 77.0$ ppm) as a reference and the coupling constant (J) in herz. Infrared spectra were recorded on a Shimadzu FTIR-8000A spectrometer and are presented in cm^{-1} . SEC was carried out with JASCO 800 HPLC system equipped with UV detector using THF as an eluent: flow rate, $1.0\text{ mL}\cdot\text{min}^{-1}$ with a Shodex column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by standard polystyrene. XRD patterns were measured with Rigaku X-RAY DIFFRACTIONMETER

RINT Ultima+/PC.

1.2.2 General Procedure for the cross-coupling reaction of siloxane with an aryl iodide in the presence of silver(I) oxide (Conditions A)

To a mixture of $[\text{Ph}(\text{Me})\text{SiO}]_n$ **1** (1.36 g, 10.0 mmol), Ag_2O (0.46 g, 2.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 5 mol%) in 3 mL of THF was added aryl iodide (2.0 mmol). After the mixture was stirred at 60 °C for 24 h, 20 mL of diethyl ether was added to the resulting mixture and stirring was continued for 10 min. The mixture was passed through a Celite pad to remove the silver residue. The pad was washed with 20 mL of diethyl ether. Concentration of the combined filtrate left a crude oil, which was chromatographed on silica gel (hexane:toluene = 10:1) to afford the corresponding coupling product.

1.2.3 General Procedure for the cross-coupling reaction of a siloxane with an aryl iodide in the presence of TBAF (Conditions B)

To a solution of **1** (0.97 g, 6.0 mmol) in 20 mL of THF was added TBAF (6 mL of 1 M THF solution, 6.0 mmol) at room temperature under an argon. To the mixture were successively added aryl iodide (5.0 mmol) and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (125 mg, 2 mol%). The solution was heated at 60 °C and the reaction was continued for 3 h. After being cooled to an ambient temperature, the resulting mixture was passed through a Celite pad. The filtrate was concentrated *in vacuo* to leave a dark brown liquid, which was purified by chromatography on silica gel to afford the corresponding coupling product.

1.2.4 General procedure for the cross-coupling reaction of a siloxane with an aryl iodide in the presence of silver(I) oxide in 1,4-dioxane (Conditions C)

To a solution of **1** (49 mg, 0.36 mmol; per unit) in 1,4-dioxane (2 mL) were added aryl iodide (0.3 mmol), Ag₂O (70 mg, 0.3 mmol) and Pd(PPh₃)₄ (17 mg, 5 mol%) under an argon atmosphere. The resulting solution was degassed via three freeze-pump-thaw cycles and heated in an oil bath at 100 °C. After the mixture was stirred for 1 h, the reaction mixture was diluted with diethyl ether and passed through a Celite pad. The plug was washed with diethyl ether and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding coupling product.

1.2.5 Poly[4-methoxyphenyl(methyl)siloxane] (**3**)

To a solution of Pd₂(dba)₃·CHCl₃ (93 mg, 1.5 mol%) and P(*o*-tol)₃ (110 mg, 6 mol%) in dry NMP (12 mL) was added 4-iodoanisole **2b** (1.4 g, 6 mmol), diisopropylentylamine (3.06 mL, 18 mmol) and PMHS (361 mg, 6 mmol; per unit). After the mixture was stirred for 16 h at 100 °C, the resulting solution was filtered off. The filtrate was concentrated under reduced pressure to leave a crude oil, which was further treated at 170 °C/0.6 mmHg to afford **3** (760 mg) as a brown oil.

SEC analysis showed M_n of 8800 ($M_w/M_n = 2.92$). ¹H NMR (300 MHz, CDCl₃): δ = 0.064-0.23 (br, 3 H), 3.75 (br, 2.58 H), 6.71 (br, 1.97 H), 7.37 (br, 2.18 H). IR (neat): ν = 2961.1, 1597.3, 1504.7, 1280.9, 1250.0, 1124.6, 1034.0 cm⁻¹.

1.2.6 Poly[methyl(4-methylphenyl)siloxane] (**4**)

Synthesis of **4** was carried out in a similar manner to that of **3**: SEC analysis showed M_n of 9600 ($M_w/M_n = 2.88$). ^1H NMR (300 MHz, CDCl_3): $\delta = 0.045\text{--}0.20$ (br, 3 H), 2.31 (br, 2.28 H), 6.97 (br, 1.92 H), 7.35 (br, 1.99 H). IR (neat): $\nu = 2964.9, 1605.0, 1261.6, 1120.8, 1022.4\text{ cm}^{-1}$.

1.2.7 Poly[methyl(2-phenylethenyl)siloxane] (**5**)

To a screw-capped tube equipped with a magnetic stirring bar were added $(\text{Bu}_4\text{N})_2\text{PtCl}_6$ (9 mg, 0.01 mmol), phenylacetylene (2.0 g, 20 mmol), and PMHS (1.2 g; 20 mmol per unit). The resulting mixture was heated at 60 °C for 24 h to form crude **5**, which was confirmed by ^1H NMR. SEC analysis showed M_n of 8500 ($M_w/M_n = 3.22$). ^1H NMR (300 MHz, CDCl_3): $\delta = -0.2\text{--}0.4$ (br, 3 H), 5.7 (br, 2 H), 5.47 (br d, $J = 20\text{ Hz}$, 1 H), 6.1 (br, 1 H).

1.2.8 Poly[methyl(1-octen-1-yl)siloxane] (**6**)

Synthesis of **6** was carried out in a manner to that of **5**. SEC analysis showed M_n of 3100 ($M_w/M_n = 1.54$). ^1H NMR (300 MHz, CDCl_3): $\delta = 0\text{--}0.3$ (br s, 3 H), 0.88 (br s, 3 H), 1.3 (br, 8 H), 2.05 (br, 2 H), 5.47 (br d, $J = 20\text{ Hz}$, 1 H), 6.1 (br, 1 H).

1.2.9 2,4,6,8-tetramethyl-2,4,6,8-tetra(2-phenylethenyl)cyclotetrasiloxane (**9**)

To a screw-capped tube equipped with a magnetic stirring bar were added $(\text{Bu}_4\text{N})_2\text{PtCl}_6$ (9 mg, 0.01 mmol), phenylacetylene (2.0 g, 20 mmol), and D_4^{H} (1.2 g; 20

mmol per unit). The resulting mixture was heated at 60 °C for 24 h to form crude **9**, which was confirmed by ^1H NMR and directly used for further reactions without purification. ^1H NMR (300 MHz, CDCl_3): δ = 0.1-0.5 (br, 12 H), 5.7-6.0 (br, 4H), 6.2-6.4 (br, 4 H), 6.8-7.6 (br, 20 H).

1.2.10 2,4,6,8-tetramethyl-2,4,6,8-tetra(1-octen-1-yl)cyclotetrasiloxane (**10**)

Synthesis of **10** was carried out in a similar manner to that of **9**. ^1H NMR (300 MHz, CDCl_3): δ = 0-0.3 (m, 12 H), 0.89 (br, 12 H), 1.2-1.5 (br, 32 H), 2.0-2.2 (br, 8 H), 5.5 (br, J = 20 Hz, 4 H), 6.1-6.3 (br, 4 H).

These compounds were used for the cross-coupling reactions without further purification.

1.2.11 1,1,1,3,5,5,5-Heptamethyl-3-phenyltrisiloxane (**11**)

To a solution of hexamethylcyclotrisiloxane (D_3) (445 mg, 2.0 mmol) in Et_2O (18 mL) was slowly added MeLi (5.77 mL, 6.0 mmol, 1.04 M in diethyl ether) at 0 °C. After the mixture was stirred at rt for 12 h, PhMeSiCl_2 (0.48 mL, 3.0 mmol) was added slowly at 0 °C. The mixture was allowed to warm to room temperature, and stirring was continued for an additional 7 h. After the organic phase was separated, the aqueous phase was extracted with diethyl ether (30 mL $\times$ 2). The combined extracts were washed with brine (30 mL), dried over magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane:ethyl acetate = 50:1) and bulb-to-bulb distillation under reduced pressure to afford **11** (116 mg, 0.39 mmol, 13%

yield). ^1H NMR (300 MHz, CDCl_3): δ = 0.103 (s, 18 H), 0.27 (s, 3H), 7.24-7.38 (m, 3 H), 7.53-7.57 (m, 2 H).

1.2.12 Measurement of the molecular weight after treatment of **5**

To a solution of **5** (39 mg; 0.24 mmol per unit) in 3 mL of THF was added TBAF (0.24 mL, 0.24 mmol as 1 M THF solution) at room temperature. The resulting mixture was stirred at room temperature for 1 h and poured into a mixture of 20 mL of diethyl ether. Two phases were separated and the aqueous layer was extracted twice with 10 mL of dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil. SEC analysis showed M_n of 2300 ($M_w/M_n=1.25$).

1.2.13 General Procedure for the cross-coupling reaction of a siloxane with an aryl chloride in the presence of K_2CO_3

To a toluene (3 mL) solution of **1** (204 mg, 1.5 mmol) was added K_2CO_3 (414 mg, 3.0 mmol) in water (0.5 mL). After stirring at rt for 1 h, 1-chloro-4-methoxybenzene **12a** (43 mg, 0.3 mmol) and $\text{PdCl}_2(\text{PCy}_3)_2$ (11 mg, 0.015 mmol) were added and then the resulting yellow mixture was stirred at 120 °C for 39 h. After cooling the mixture to rt, the organic layer was separated and aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layer was washed with 1 M HCl (10 mL), sat. aq NaHCO_3 (10 mL), and brine (10 mL), and then dried over anhydrous MgSO_4 . Removal of the solvent left a crude oil, which was purified by chromatography on silica gel (reverse phase,

MeOH:H₂O = 3:1) to yield 52.5 mg of 4-methoxy-biphenyl (95%).

1.2.14 Preparation of a sample for XRD analysis

The procedure described for the cross-coupling reaction was followed using **1** (49 mg, 0.36 mmol; per unit), 4-iodoanisole **2b** (70 mg, 0.3 mmol), Pd(PPh₃)₄ (17 mg, 5 mol%), and Ag₂O (70 mg, 0.3 mmol). The mixture involving a black precipitate was filtered off and washed with ethanol and then diethyl ether. The resulting solid was dried under reduced pressure to give a black powder, which was subjected to a glass plate for the XRD analysis and set in the diffractometer. The results were shown below.

1.2.15 Residue with the cross-coupling reaction of a polysiloxane **1** with a **2b**

2θ (rel intensity): 22.393, 23.729, 25.364, 32.846, 39.250, 42.692, 45.648, 46.364.

1.2.16 Ag₂O for XRD analysis

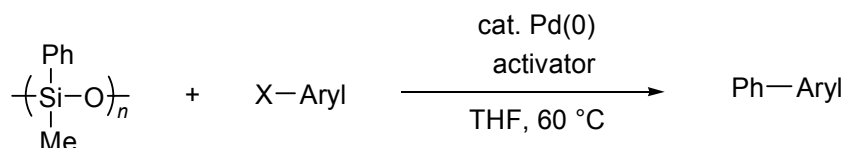
2θ (rel intensity): 7.718 (927), 8.478 (502), 9.640 (221), 12.841 (263), 21.321 (433), 22.360 (757), 23.259 (234), 23.702 (1777), 25.320 (329), 25.905 (136), 28.941 (209), 32.857 (357), 39.200 (1308), 42.640 (284), 46.320 (630).

1.2.17 AgI for XRD analysis

2θ (rel intensity): 23.070 (100), 39.133 (60), 46.308 (30), 56.667 (6), 62.258 (8), 71.028 (8), 76.082 (6), 84.285 (4), 89.100 (4), 97.186 (4), 125.101 (4).

1.3 Results and Discussion

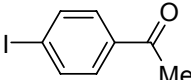
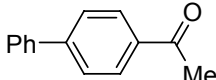
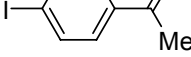
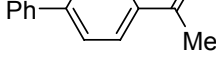
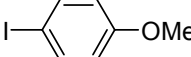
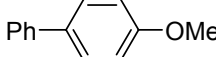
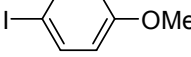
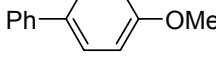
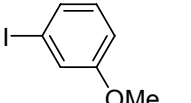
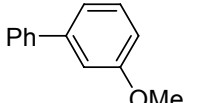
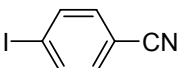
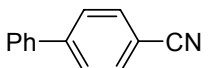
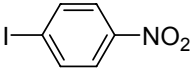
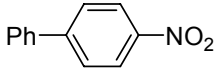
We first examined the reaction of a polysiloxane bearing a phenyl group, which was commercially available as a highly thermo-resistant silicone oil (Scheme 1).



Scheme 1. Cross-coupling reaction of silicone with aryl halides.

The results are summarized in Table 1. The reaction with an aryl iodide was examined using silver(I) oxide (Ag_2O) or tetrabutylammonium fluoride (TBAF). We have previously shown that Ag_2O is an effective activator for the cross-coupling reaction of silanols and silanediols.^{3g,3h} TBAF has also been employed frequently for the cross-coupling reaction of organofluorosilanes di- or trifluorosilanes and silanols³. The reaction of poly(methylphenylsiloxane) **1** with 4-iodoacetophenone **2a** in the presence of 5 mol% of $\text{Pd}(\text{PPh}_3)_4$ and Ag_2O at 60 °C in THF for 20 h afforded the corresponding coupling product in 67% yield (Conditions A). TBAF was also found to be an efficient activator for the coupling reaction, which proceeded with 2.5 mol% of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (Conditions B). Under these conditions, aryl iodides bearing an electron-donating or -withdrawing substrate on the aromatic ring underwent the coupling reaction in good yields.^{4a}

Table 1. Cross-coupling of a polysiloxane **1** with iodides in THF ^a

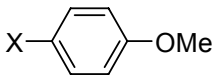
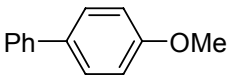
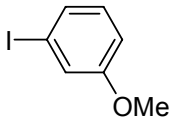
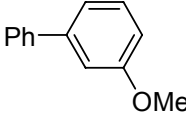
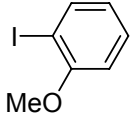
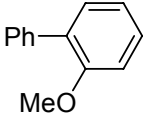
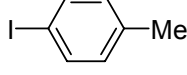
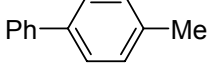
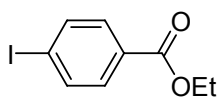
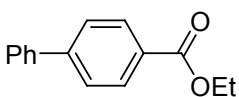
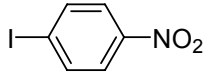
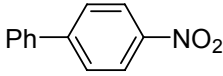
entry	I–Aryl	activator ^b	time/h	product	%yield ^c
1	 (2a)	Ag ₂ O	20		67
2	 (2a)	TBAF	20		53
3	 (2b)	Ag ₂ O	20		52
4	 (2b)	TBAF	20		79
5	 (2c)	Ag ₂ O	24		96
6	 (2d)	Ag ₂ O	24		59
7	 (2e)	Ag ₂ O	24		97

(a) The reaction was carried out at 60 °C in THF (3 mL) using **1** (1.0 mmol; per unit) or **2** (0.2 mmol) and aryl iodide (0.2 mmol). (b) Conditions A: Pd(PPh₃)₄ (5 mol%), Ag₂O (0.2 mmol), conditions B: Pd₂(dba)₃·CHCl₃ (2.5 mol%), TBAF (0.24 mmol). (c) Isolated yield based on the aryl iodide.

Although cross-coupling of silicone **1** was found to proceed in THF at 60 °C, the reaction was required to use excess amounts of **1** toward the aryl iodide. However, further optimization of reaction conditions revealed to achieve the reaction with a smaller amount of **1**. The reaction completed within a shorter reaction period when the coupling reaction was carried out at higher temperature with 1,4-dioxane as a solvent. As summarized in Table 2, 1.2 equiv of polysiloxane **1** reacted with various aryl iodides in 1,4-dioxane at 100 °C (Conditions C). The reaction of aryl iodides bearing an electron-donating or electron-withdrawing substituent on the phenyl ring afforded the

corresponding coupling products in good yields. Aryl iodides bearing a substituent at the 2- or 3-position were also found to tolerate to give the coupling product in good yields (entries 5 and 6).

Table 2. Cross-coupling reaction of polysiloxane **1** with aryl halides in 1,4-dioxane^a

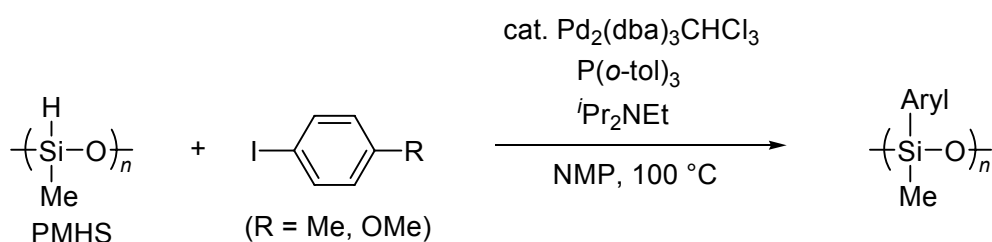
entry	X-Aryl		time/h	product	%yield
1		X = I	1		71
2			1		64 ^b
3		Br	44		<2
4		Cl	72		0
5			1		64
6			1		65
7			1.5		73
8			1.5		74
9			1.5		57
10			24		96 ^c

(a) The reaction was carried out at 100 °C using **1** (0.36 mmol; per unit), aryl iodide (0.3 mmol), Ag₂O (0.3 mmol), and Pd(PPh₃)₄ (5 mol%) in 2 mL of 1,4-dioxane (Conditions C).

(b) The reaction was carried out at 100 °C using **1** (2.4 mmol; per unit), aryl iodide (2.0 mmol), Ag₂O (2.0 mmol), and Pd(PPh₃)₄ (5 mol%).

(c) The reaction was carried out at 60 °C in THF (3 mL) using **1** (1.0 mmol; per unit), aryl iodide (0.2 mmol), Ag₂O (0.2 mmol), and Pd(PPh₃)₄ (5 mol%).

In addition to the polysiloxane **1**, which was a readily available reagent, our concern was then turned to the reaction of silicone reagents of several other aryl groups. Although polysiloxanes bearing a substituted aryl group are not available commercially, such compounds can be synthesized using a commercially available polysiloxane bearing a silicon-hydrogen bond, PMHS⁵ by employing the palladium-catalyzed arylation of triethoxysilane with aryl iodides developed by Masuda.⁶ The method was applied for the arylation of PMHS as a silane species. As shown in Scheme 2, the arylation of PMHS with 4-iodoanisole or 4-iodotoluene using 2.5 mol% of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ as a catalyst proceeded to afford the corresponding coupling product poly[methyl(4-methoxyphenyl)siloxane] **3** or poly[methyl(4-methylphenyl)siloxane] **4** smoothly. Contents of arylation in the crude product were estimated by ^1H NMR indicating to be 85% and 75%, respectively.

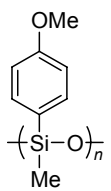
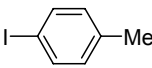
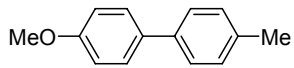
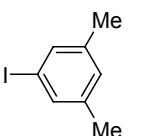
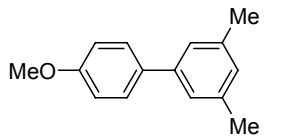
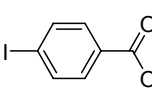
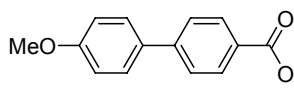
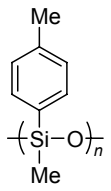
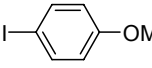
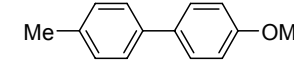
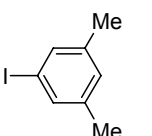
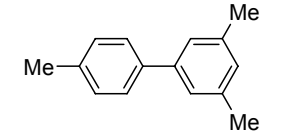
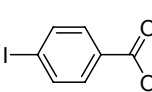
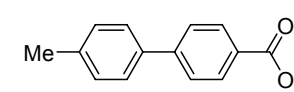


Scheme 2. Palladium-catalyzed Arylation of PMHS with aryl iodides.

Although the attempted purification of the arylated polysiloxane was unsuccessful, the cross-coupling reaction with the crude polysiloxane was found to produce the corresponding coupling products. In addition, these polysiloxane could be stored under

an aerobic condition at room temperature for several months. Indeed, the obtained **3** and **4** were subjected to the palladium-catalyzed cross-coupling reactions with several aryl iodides in the presence of silver(I) oxide to afford the corresponding biaryls in moderate to good yields. These results are summarized in Table 3.

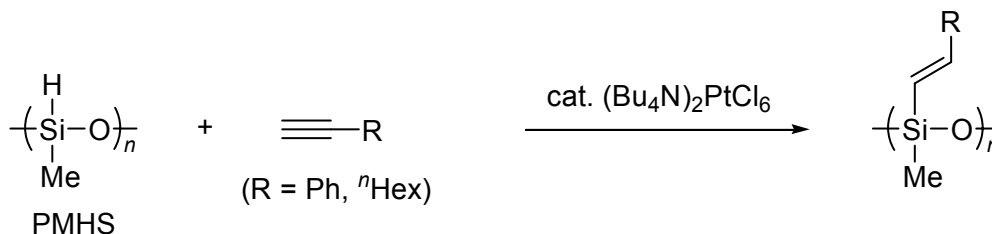
Table 3. Cross-coupling reaction of poly(arylsiloxane)s with aryl iodides^a

entry	silicone	I-Aryl	time/h	product	%yield
1	 (3)	 (2g)	4		67
2		 (2i)	10		52
3		 (2h)	1		94
4	 (4)	 (2b)	5		41
5		 (2i)	22		25
6		 (2h)	24		56

(a) The reaction was carried out using **3** or **4** (0.3 mmol; per unit), aryl iodide (0.3 mmol), Ag₂O (0.3 mmol), and Pd(PPh₃)₄ (5 mol%) in 2 mL of 1,4-dioxane.

Polysiloxanes bearing an alkenyl group were also found to be obtained easily from PMHS. The hydrosilylation of a terminal alkyne with PMHS using a catalytic amount

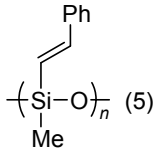
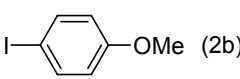
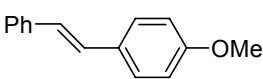
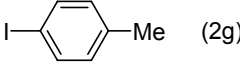
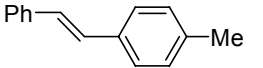
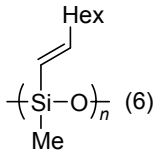
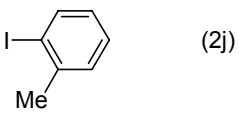
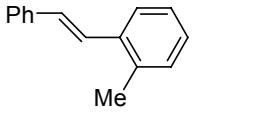
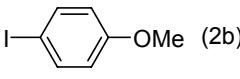
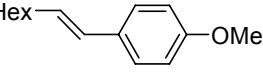
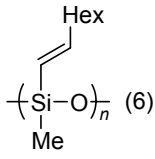
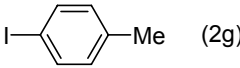
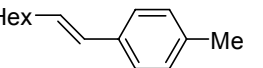
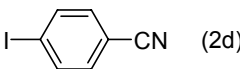
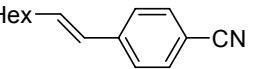
of $(\text{Bu}_4\text{N})_2\text{PtCl}_6$ ⁷ proceeded smoothly to afford poly[methyl(2-phenylethenyl)siloxane] **5** or poly[methyl(1-octen-1-yl)siloxane] **6** as shown in Scheme 3.



Scheme 3. hydrosilylation of a terminal alkyne with PMHS.

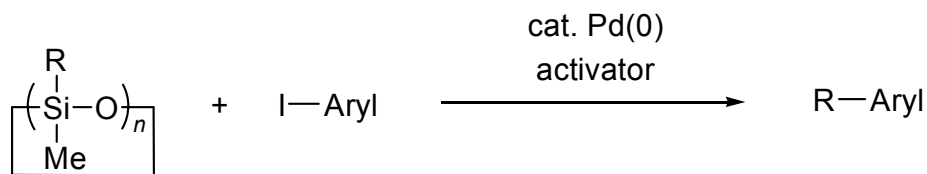
Measurement of ^1H NMR showed that the alkenyl group was introduced in a quantitative manner although the attempted purification of polysiloxanes **5** and **6**, which were stored at an ambient temperature in air, was not successful. The obtained **5** or **6** were employed for the palladium-catalyzed coupling reactions as shown in Table 4. TBAF was found to be a suitable activator in the coupling of alkenysiloxanes, which took place faster than that of phenylsiloxanes. Indeed, the reaction of alkenysiloxane proceeded within 1-2 h to give the desired products in excellent yields. The coupling reaction with use of a slight excess (1.2 equiv) of siloxanes also underwent smoothly.

Table 4. Cross-coupling reaction of poly(alkenylsiloxane)s with aryl iodides ^a

entry	silicone	I-Aryl	time/h	product	%yield
1	 (5)	 (2b)	1		80 (>99) ^b
2			1		94 ^c
3		 (2g)	1		>99
4	 (6)	 (2j)	1		97
5			1		90 (>99) ^b
6		 (2b)	1		98 ^c
7	 (6)	 (2g)	1		51 (>99) ^b
8		 (2d)	2		90

(a) Unless otherwise noted, the reaction was carried out using 1.0 mmol (5 equiv per unit) of **5** or 0.2 mmol of **6**, 0.2 mmol of aryl iodide, 0.24 mmol of TBAF, and 5 mol% of Pd₂(dba)₃·CHCl₃ at 60 °C in 3 mL of THF. (b) Isolated yield by silica gel chromatography. The yield estimated by ¹H NMR is given in parentheses. (c) The amount of employed polysiloxanes was 0.24 mmol (1.2 equiv per unit).

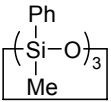
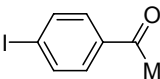
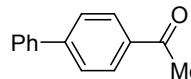
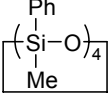
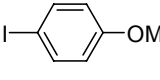
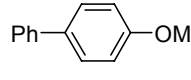
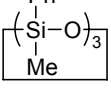
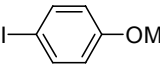
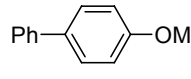
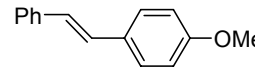
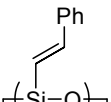
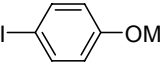
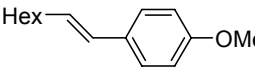
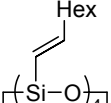
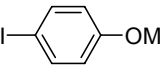
In addition to the polysiloxanes, a commercially available cyclic siloxane bearing phenyl groups, 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane; (D₃^{Ph}) **7** or 2,4,6,8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane; (D₄^{Ph}) **8**, which had been used as a precursor of silicone polymers by ring opening polymerization¹, was also found to be reactive in the coupling reaction (Scheme 4).



Scheme 4. Cross-coupling reaction of cyclic siloxane with aryl iodides.

Denmark reported vinyl-substituted cyclic oligosiloxanes are the effective vinylation reagents of aryl and alkenyl iodides in the presence of TBAF.⁸ Recently, Fugami also reported cross-coupling reaction of hexaarylcyclotrisiloxane by the addition of aqueous potassium hydroxide in good yield.⁹ The high temperature afforded the corresponding coupling product within 1 h (entry 4). This temperature dependence was closely similar to the reactivity of polysiloxane. Furthermore, a cyclic siloxane bearing alkenyl groups, 2,4,6,8-tetramethyl-2,4,6,8-tetra(2-phenylethenyl)cyclotetrasiloxane **9** (R=Ph) and 2,4,6,8-tetramethyl-2,4,6,8-tetra(1-octen-1-yl)cyclotetrasiloxane **10** (R=Hex) were synthesized by the similar hydrosilylation with the corresponding cyclic hydrosiloxane, 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^{H}). The reaction of cyclic siloxane bearing alkenyl groups at 60 °C proceeded within 1-3 h to afford corresponding coupling product in excellent yield (entries 5-9). Under these conditions, the reactivity of cyclic siloxanes bearing alkenyl groups was much higher than that of phenyl groups. A palladium catalyst with $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ without phosphine ligand was found to be equally effective for the coupling of alkenylsiloxanes (entries 7 and 9). These results are summarized in Table 5.

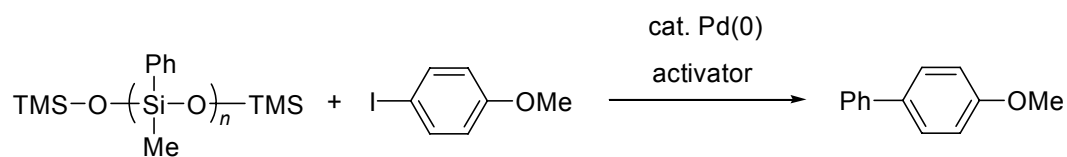
Table 5. Cross-coupling reaction of cyclic siloxanes with aryl iodides ^a

$ \begin{array}{c} \text{R} \\ \\ (\text{Si}-\text{O})_n \\ \\ \text{Me} \end{array} + \text{I}-\text{Aryl} \xrightarrow[\text{activator}]{\text{cat. Pd(0)}} \text{R}-\text{Aryl} $							
entry	silicone	I-Aryl	activator	temp/°C	time/h	product	%yield
1	 (7)	 (2a)	Ag ₂ O	60	24		55
2			TBAF	60	40		36
3	 (8)	 (2b)	Ag ₂ O	60	120		39
4			Ag ₂ O	100	1		75
5	 (9)	 (2b)	Ag ₂ O	100	1.5		65
6			TBAF	60	1		99
7	 (10)	 (2b)	TBAF	60	1		85 ^b
8			TBAF	60	1		88
9	 (10)	 (2b)	TBAF	60	1		79 ^b
10			TBAF	60	3		96 ^c

(a) Unless otherwise noted, the reaction was carried out using 1.0 mmol (5 equiv per unit) of 0.2 mmol of cyclic siloxane of aryl iodide, 0.24 mmol of activator, and 5 mol% of Pd₂(dba)₃·CHCl₃ at 60 °C in 3 mL of THF. (b) The reaction was carried out at 100 °C in 1,4-dioxane. (c) The amount of employed siloxane was 0.24 mmol (1.2 equiv per unit). (d) 5 mol% of Pd(PPh₃)₄ was used as a palladium catalyst.

Cross coupling of silicone of different degrees of polymerization, whose terminal was protected with the trimethylsilyl group, was carried out with **2b**. Employing the average molecular weight of 2500-2700 (approx. 20 mer), 700-900 (approx. 6 mer), and 350-450 (approx. 2 mer) cross-coupling was examined. These results are summarized in Table 6. The yield of the reaction with Ag₂O as an activator was found to decrease as

the degree of polymerization is smaller when 1.2 equiv of silicone toward **2b** was used. However, the reaction with 2 equiv of silicone afforded the corresponding biaryl in good yield irrespective of the degree of polymerization (entries 4 and 7). We then examined the reaction of phenyltrisiloxane **11**, whose terminals are trimethylsilyl groups, with 1.2 and 2 equivalents of **2b** (entries 9 and 10). Under similar conditions to polysiloxanes, the reactions were found to afford coupling product in rather lower yields. The results suggest that the activation of silicone with Ag₂O hardly occurs at the trimethylsilylated end group. On the other hand, the cross-coupling reaction of trimethylsilylated disiloxane has been shown to occur by Denmark¹⁰ when TBAF was employed as an activator. Indeed, the reaction of silicone with different degrees of polymerization was found to show little influence for the reactivity.

Table 6. Cross-coupling reaction of silicone of different degrees of polymerization ^a

entry	silicone	M_w	activator	equiv of Ph	time/h	%yield
1	$\left(\text{Si}\begin{array}{c} \text{Ph} \\ \\ \text{O} \\ \\ \text{Me} \end{array}\right)_{20}$	2500-2700	Ag ₂ O	1.2	1	71
2			TBAF	3.0	1.5	59
3	$\left(\text{Si}\begin{array}{c} \text{Ph} \\ \\ \text{O} \\ \\ \text{Me} \end{array}\right)_6$	700-900	Ag ₂ O	1.2	1.5	62
4			Ag ₂ O	2.0	1	72
5			TBAF	3.0	19	63
6	$\left(\text{Si}\begin{array}{c} \text{Ph} \\ \\ \text{O} \\ \\ \text{Me} \end{array}\right)_2$	350-450	Ag ₂ O	1.2	2	56
7			Ag ₂ O	2.0	1.5	73
8			TBAF	1.2	1.5	60
9	$\left(\text{Si}\begin{array}{c} \text{Ph} \\ \\ \text{O} \\ \\ \text{Me} \end{array}\right)_1$ (11)	298	Ag ₂ O	1.2	24	15
10			Ag ₂ O	2.0	24	13

(a) Unless otherwise noted, the reaction was carried out using silicone, 4-iodoanisole **2b** (0.3 mmol), activator (0.3 mmol), and Pd(PPh₃)₄ (5 mol%) in 2 mL of 1,4-dioxane.

When polyalkenylsiloxane **5** ($M_n = 8500$) was treated with TBAF and stirred at room temperature for 1 h, size exclusion chromatography (SEC) analysis of the resulting mixture showed the number average molecular weight (M_n) of 2300. The result indicates that polysiloxanes would be cleaved into smaller segments but not converted completely to monomeric species. Accordingly, we consider that a certain oligomer

would be involved by the activation with TBAF in the cross-coupling reaction. On the contrary, the molecular weight did not change after treated with Ag_2O even at $100\text{ }^\circ\text{C}$.

Recently, we reported the plausible reaction mechanism in the cross-coupling reaction of silanols with an aryl iodide.³ⁱ In the reaction of silanols, silver oxide would interact with intermediary organopalladium(II) iodide complex produced by the oxidative addition of aryl iodide to palladium(0) due to the strong affinity of iodine with silver. Silver oxide may act as a nucleophilic activator of silicone to form pentacoordinate silicate species, which also facilitate the transfer of an organic group on silicon to palladium (transmetalation). In case of polysiloxane, similar intermediate seem to be generated in the reaction system. XRD analysis showed existence of AgI in the reaction mixture. The plausible reaction mechanism is illustrated in Figure 1.

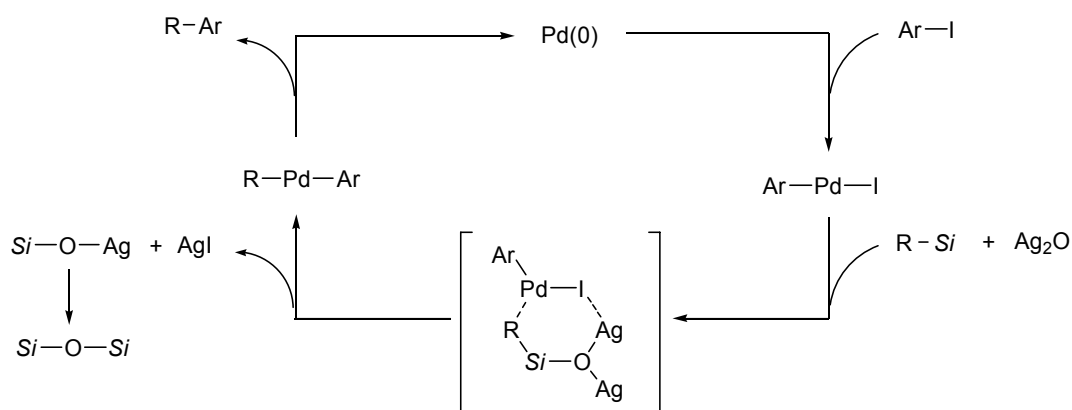
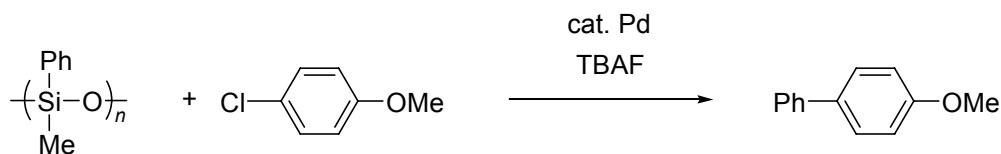


Figure 1 Plausible mechanism of the cross-coupling reaction with an Organosilicon reagent.

Since aryl chlorides are one of the most attractive substrates for the transition metal-catalyzed cross-coupling reaction due to the lower cost compared to aryl bromide or aryl iodide counterparts¹¹, our focus was directed to modify the reaction protocol of silicone in order to cross-couple with aryl chlorides. These results are summarized in Table 7.

The reaction of **1** with 1-chloro-4-methoxybenzene **12a** in the presence of 5 mol% of $\text{PdCl}_2(\text{PCy}_3)_2$ ¹², which possessed electron-donating and bulky phosphine ligands and was shown to be effective for several cross-coupling reaction of aryl chlorides, was first examined using TBAF as an activator (Scheme 5).^{4b}



Scheme 5. Cross-coupling reaction of silicone with aryl chloride.

According to the procedure for the cross-coupling of aryl iodides, the reaction was carried out using an equimolar amount of TBAF relative to the silicon atom of **1** in toluene at 120 °C for 39 h. However, no coupling product was obtained at all (entry 1). Dramatic improvement was observed by addition of water to afford the desired cross-coupling product in 65% yield (entry 2). Moreover, it is effective to stir the silicone **1** in the presence of TBAF/ H_2O at rt for 1 h before the addition of the palladium catalyst and **12a** to accomplish the cross-coupling reaction giving coupling product in

78% yield (entry 3). On the other hand, the coupling reaction did not proceed with the palladium catalyst in the absence of a phosphine ligand and in the presence of triphenylphosphine (entries 4 and 5). These results are explained in terms of the lower reactivity of aryl chlorides compared to that of aryl iodides toward a palladium complex.^{10,11a-d} Ethereal solvent such as 1,4-dioxane was similarly effective for the biaryl formation to furnish the desired coupling product in 81% yield (entry 6). Lowering the temperature to 70 °C also caused cross-coupling to give coupling product in 46% yield (entry 7) and increasing the amount of TBAF (2 equiv) resulted in lowering the yield of coupling product (entry 8).

Table 7. Palladium-catalyzed cross-coupling reaction of **1** with 1-chloro-4-methoxybenzene^a

entry	cat. Pd	solvent	temp/°C	activator	%yield ^b
1	PdCl ₂ (PCy ₃) ₂	toluene	120	TBAF	0
2	PdCl ₂ (PCy ₃) ₂	toluene	120	TBAF/H ₂ O	65
3	PdCl ₂ (PCy ₃) ₂	toluene	120	TBAF/H ₂ O	78 ^c
4	Pd ₂ (dba) ₃	toluene	120	TBAF/H ₂ O	0 ^d
5	Pd(PPh ₃) ₄	toluene	120	TBAF/H ₂ O	0
6	PdCl ₂ (PCy ₃) ₂	1,4-dioxane	100	TBAF/H ₂ O	81
7	PdCl ₂ (PCy ₃) ₂	1,4-dioxane	70	TBAF/H ₂ O	46
8	PdCl ₂ (PCy ₃) ₂	1,4-dioxane	100	TBAF/H ₂ O	61 ^e

(a) Unless otherwise noted, the reaction was carried out using **1** (1.5 mmol/unit), **12a** (0.3 mmol), 5 mol% of palladium catalyst, and TBAF (1.5 mmol) in the presence of water (0.5 mL) for 39 h. (b) The yield was determined by ¹H NMR using diphenylmethane as an internal standard. (c) Stirring **1** with TBAF at rt for 1 h before starting reaction. (d) Pd₂(dba)₃·CHCl₃ (2.5 mol%) was employed. (e) TBAF (3.0 mmol) was used.

Screening of fluoride-free¹³ additive for the cross-coupling reaction revealed that Cs₂CO₃ or K₂CO₃ served as an effective activator as summarized in Table 8. The reaction in the presence of CsCO₃ produced the cross-coupling product in 73% yield (entry 1). It should be pointed out that use of K₂CO₃ lead to the complete consumption of **12a** to afford the corresponding coupling product in a quantitative yield (entry 3).

The reaction with K_2CO_3 proceeded at higher temperature (100 °C) in 1,4-dioxane (entry 5). Another inorganic activator such as NaOH was also found to be applicable (entry 6). On the other hand, no coupling product was obtained when Ag_2O was employed (entry 7). This result is ascribed to the inferior interaction ability between silver and chlorine atom compared with the iodide case. Decreasing the amount of K_2CO_3 from 2.0 equivalents to 1.0 equivalent relative to **1** was found to be less effective to afford a smaller amount of the cross-coupling product (entry 2). Similarly, the reaction was suppressed to some extent with increasing the amount of K_2CO_3 from 2.0 equivalents to 3.0 equivalents (entry 4) suggesting that the reaction was significantly influenced by the amount of activator employed.

Table 8. Effect of additive in the cross-coupling of silicone **1**^a

entry	additive	additive/silicone	%yield ^b
1	Cs ₂ CO ₃	2	73
2	K ₂ CO ₃	1	65
3	K ₂ CO ₃	2	>99
4	K ₂ CO ₃	3	70
5	K ₂ CO ₃	2	64
6	NaOH	2	>99
7	Ag ₂ O	1	0

(a) Unless otherwise noted, the reaction was carried out in 3 mL of toluene and 0.5 mL of water for 39 h at 120 °C using silicone (1.5 mmol; per unit), aryl chloride (0.3 mmol), 5 mol% of PdCl₂(PCy₃)₂, and additive. (b) The reaction yield was estimated by ¹H NMR. (c) The reaction was carried out at 100 °C in 1,4-dioxane.

Various aryl chlorides were treated with **1** to provide the corresponding coupling products in moderate to excellent yields. As illustrated in Table 9, aryl chlorides bearing an electron-donating or electron-withdrawing substituent on the aromatic ring underwent the cross-coupling reaction in good yields. Sterically hindered aryl chloride **12c** was also tolerated to produce the corresponding product in 43% yield (entry 2). A heteroaromatic substrate such as 2-chloroquinoline **12g** reacted to afford corresponding coupling product in 68% yield (entry 6). Furthermore, **5** also served as a substrate for

the alkenylation to afford stilbene derivatives in good yields (entries 7 and 8).

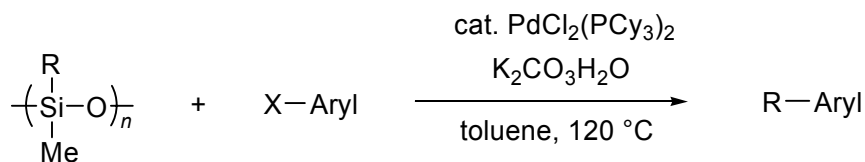
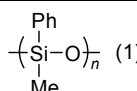
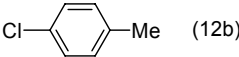
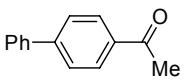
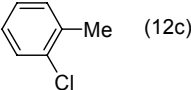
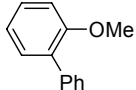
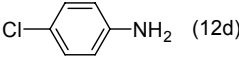
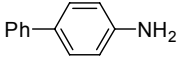
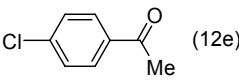
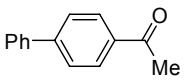
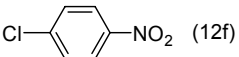
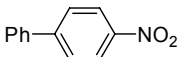
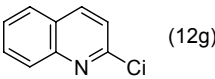
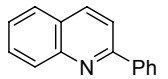
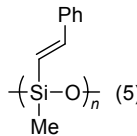
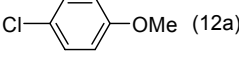
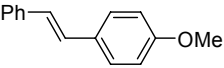
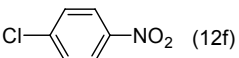
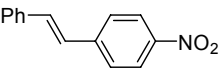


Table 9. Cross-coupling of silicone with various aryl chlorides ^a

entry	silicone	Cl-Aryl	product	%yield ^b
1	 (1)	 (12b)		92
2		 (12c)		43
3		 (12d)		53
4		 (12e)		>99
5		 (12f)		77
6		 (12g)		68
7	 (5)	 (12a)		97
8		 (12f)		70

(a) Unless otherwise noted, the reaction was performed in toluene (3 mL) for 29-48 h at 120 °C using silicone (1.5 mmol; per unit), aryl chloride (0.3 mmol), 5 mol% of PdCl₂(PCy₃)₂, and 3 mmol of K₂CO₃·H₂O. (b) The yield was determined by ¹H NMR analysis using diphenylmethane as an internal standard.

1. 4 Conclusion

In conclusion, silicone bearing an aryl and alkenyl groups was revealed to be available as a practical organosilicon reagent for the palladium-catalyzed cross-coupling reactions. In particular, poly(methylphenylsiloxane), which is a highly thermally stable silicone oil, allows the coupling reaction with aryl halides leading to biaryls efficiently. Polysiloxanes with a different molecular weight and several cyclic siloxanes bearing a phenyl group were also subjected to the cross-coupling. Furthermore, siloxanes with other aryl group and alkenyl group were found to be synthesized from PMHS and to be subjected to the palladium-catalyzed coupling reactions. Silver(I) oxide, TBAF, and aqueous K_2CO_3 serves as an effective activator for the silicone reagents. Organic synthesis with a transition metal-catalyst is a new class of utilization of silicone, which is an environmentally friendly and less expensive reagent.

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Chapter 2

Syntheses and Electrochemical Properties of TEMPO Radical

Substituted Silicones: Active Material for Organic Radical Batteries

Abstract: A silicone-based radical polymer, poly[methyl(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxypropyl)siloxane] **2** was synthesized by hydrosilylation of poly(methylhydrosiloxane) (PMHS) with 4-allyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl ether **1** in the presence of a platinum- or rhodium-catalyst. A reversible redox peak of **2** at 3.56 V (vs. Li/Li⁺) was observed by CV measurements. The coin-shaped cell of **2** shows the discharge capacity of 46 mAh·g⁻¹, which is 47% of the theoretical capacity of the polymer **2** (98 mAh·g⁻¹). A directly TEMPO-substituted silicone, poly[methyl(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxy)siloxane] **3** was also obtained by rhodium-catalyzed dehydrogenative alcoholysis of PMHS with TEMPO-OH. The coin-shaped cell of **3** shows a discharge capacity of 80 mAh·g⁻¹, which is 69% of the theoretical capacity of **3** (116 mAh·g⁻¹).

2.1 Introduction

Lithium-ion batteries are widely used in portable electronic devices such as cellular phones and laptop computers; however, the use of LiCoO_2 , which is used as a cathode active material for lithium-ion batteries, presents cost, toxicity, and underresourcing problems.¹ In particular, the cost and production of lithium-ion batteries are strongly affected by the cobalt supply. Since lithium-ion batteries will be used for electric vehicles, there is growing concern about the depletion of cobalt resource.

In contrast, silicon compounds are present in great quantity in the earth and are easily obtainable. In other word, the sustainable supply of silicon compounds is guaranteed. Silicone, which is a polysiloxane bearing organic substituents on the silicon atom, is well known as one of the most stable organic compounds for chemical and thermal alteration.² A number of silicones with various organic substituents are readily available,³ and have been utilized in organic synthesis.⁴ However, silicones have not been used as a backbone polymer of the electrode active materials.

We have explored the use of organic radical species, in particular pendant nitroxide radical polymers, as a cathode active material for lithium-ion batteries, which is referred to as “Organic radical battery (ORB)”.⁵ These polymers contain a 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical moiety. Organic materials rather than transition metal oxides as a cathode active material of rechargeable batteries make them more environmentally friendly and easily-obtainable.⁶ Although a number of organic radical polymers have been reported so far⁷, there is no study of the silicone-based radical polymer.

We report research on charge/discharge behaviors of TEMPO-substituted silicone as a cathode active material. We also describe the fabrication of a composite electrode consisting of silicone and vapor-grown carbon fiber (VGCF), electrochemical studies by cyclic voltammetry (CV) measurements, and the charge/discharge characteristics of a Li/silicone coin-shaped cell.

2.2 Experimental

Experimental Part

Materials

All organic reactions were performed under an argon atmosphere, and chemicals were purchased and used as-is unless otherwise noted. Hexane, dry toluene, acetone, tetrahydrofuran (THF), chloroform (CHCl_3), allyl bromide, anhydrous magnesium sulfate (MgSO_4), sodium hydride (NaH), chlorotris(triphenylphosphine)rhodium(I) ($\text{RhCl}(\text{PPh}_3)_3$), and chloro(1,5-cyclooctadiene)rhodium(I), dimer ($[\text{RhCl}(\text{cod})]_2$) were purchased from Kanto Chemical Co., Inc. Before using the sodium hydride, we washed it with hexane to remove paraffin oil. 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO-OH), chloro(norbornadiene)rhodium(I), dimer ($[\text{RhCl}(\text{nbd})]_2$), and bis(norbornadiene)rhodium(I) tetrafluoroborate $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ were purchased from Tokyo Kasei Kogyo Co. Ltd. Potassium hexachloroplatinate (K_2PtCl_6) was purchased from Tanaka Kikinzoku Kogyo K. K. Bis(tetrabutylammonium) hexachloroplatinate(IV) ($(\text{Bu}_4\text{N})_2\text{PtCl}_6$) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst), solution in xylenes (2%Pt), bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate $[\text{Rh}(\text{cod})_2]\text{BF}_4$, and poly(methylhydrosiloxane) (PMHS) were purchased from Aldrich Chemicals Co. Ltd. Polytetrafluoroethylene (PTFE) was purchased from DAIKIN Industries. Vapor-grown carbon fibers (VGCFs) were purchased from Showa Denko. K. K. A polyethylene-film separator (#2400) was purchased from Celgard Inc. A solution containing $1 \text{ mol}\cdot\text{L}^{-1}$ of lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of ethylene carbonate (EC)/diethyl

carbonate (DEC) (3:7 vol%) was purchased from Ube Industries Inc.

General

Infrared attenuated total reflectance (IR-ATR) absorption spectra were measured using a Nicolet NEXUS 470 FT-IR spectrometer. Elemental analyses (EA) were recorded using EL and HERAEUS CHN-O RAPID elemental analyzers. ^1H and ^{13}C NMR spectra were measured using a Bruker AVANCE 400 spectrometer. The chemical shifts were recorded in parts per million downfield from tetramethylsilane ($\delta = 0$ ppm) or based on residual CHCl_3 ($\delta = 7.26$ ppm) as an internal standard. ^{13}C NMR spectra were recorded at 100 MHz with CDCl_3 as a solvent, with the central line of the solvent ($\delta = 77.0$ ppm) as a reference, and with the coupling constant (J) in hertz. Electron spin resonance (ESR) measurements were performed using a JEOL JES-FR30 spectrometer system at room temperature. Spin concentration was computed from the absorption-area intensity obtained by double integration of a first-order-derivative type of ESR spectrum. The thickness of the composite electrode was measured using a Mitsutoyo ID-C112C thickness gauge. Cyclic voltammetry (CV) measurements were performed in a dry room (dew point ≤ -50 °C) using a CH Instruments CHI 604 electrochemical analyzer. The charge/discharge measurements were performed using a Keisokuki Center Battery Labo System, BLS5500 Series.

Synthesis of allyl ether (1)

We prepared 4-allyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl ether **1** as follows: Sodium

hydride (20.9 g, 871.5 mmol) was added to a mixture of TEMPO-OH (100 g, 0.58 mmol) in 300 mL of dry THF, and the reaction mixture was stirred at room temperature for 1 h. Allyl bromide (280 g, 2.3 mol) was then added, and the mixture was stirred at room temperature for another 15 h. After the reaction, pure water (100 mL) was added to the mixture to decompose the excess NaH. The mixture was concentrated by rotary evaporation and then extracted with CHCl_3 . The extract was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The crude product was purified at 60 °C *in vacuo* to yield monomeric **1** as a high-viscosity liquid in 98% yield (121 g, 0.57 mmol).

Infrared attenuated total reflectance (IR-ATR) (Ge, cm^{-1}): 3081($\nu=\text{C-H}$), 2974 ($\nu\text{C-H}$), 2943, 2939 ($\nu\text{C-H}$), 2870 (νCH_2), 1714, 1670, 1647 ($\nu\text{C}=\text{C}$), 1464, 1429, 1377, 1364, 1350, 1242, 1220 ($\nu\text{C-O-C}$), 1192, 1176, 1134, 1086 ($\nu\text{C-O-C}$), 924 ($\nu=\text{C-H}$). $\text{C}_{12}\text{H}_{22}\text{NO}_2$: Calcd. C 67.9, H 10.4, N 6.60; Found C 67.4, H 10.5, N 6.3. ^1H NMR (400 MHz, CDCl_3 , δ): 1.23 (s, 6H, CH_3), 1.28 (s, 6H, CH_3), 1.53–1.59 (m, 2H, CH), 1.98–2.02 (m, 2H, CH), 3.70 (m, 1H, CH_2OCH_2) 4.05 (m, 2H, $\text{CH}_2=\text{CHCH}_2\text{OCH}$), 5.22–4.24 (m, 1H, $\text{H}_2\text{C}=\text{CH-O}$), 5.34–5.38 (m, 1H, $\text{H}_2\text{C}=\text{CH-O}$), 5.97–6.01 (m, 1H, $\text{CH}_2=\text{CHCH}_2$). ^{13}C NMR (100 MHz, CDCl_3 , δ): 20.2 (CMe_2), 31.8 (CMe_2), 44.4 (NCMe_2), 58.4 (OCHCH_2), 60.0 (OCH), 68.4 ($\text{H}_2\text{C}=\text{CH-CH}_2\text{O}$), 115.8 ($\text{H}_2\text{C}=\text{CHCH}_2$), 135.0 ($\text{H}_2\text{C}=\text{CHCH}_2$).

Synthesis of polymer (2)

Poly[methyl(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxypropyl)siloxane] **2** was

prepared as follows. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylenes (380 mg, 0.02 mmol; 0.2 mol%) and PMHS (625 mg, 10.4 mmol) were added to a solution of **1** (3.3 g, 15.6 mmol) in 50 mL of dry toluene. After this mixture was stirred at 100 °C for 3 h, the solvent was removed by rotary evaporation and excess **1** was removed from the crude product by washing it three times with 300 mL of hexane. The residue was dried under reduced pressure at 50 °C to afford **2** as a pale red solid (76% yield) whose color was due to the TEMPO radical. (IR-ATR) (Ge, cm^{-1}): 2976 ($\nu\text{C-H}$), 2943 ($\nu\text{C-H}$), 2883 (νCH_2), 1470, 1429, 1363, 1350, 1269, 1086 ($\nu\text{C-O-C}$), 1018 ($\nu\text{Si-O}$). $(\text{C}_{11}\text{H}_{20}\text{NO}_2)_n$: Calcd. C 57.3, H 9.62, N, 5.14; Found C 50.7, H 8.61, N 3.94 (76% hydrosilylated). Since **2** was barely soluble in THF, CHCl_3 , and DMF, its molecular weight could not be estimated by size exclusion chromatography (SEC).

Synthesis of polymer (3)

Poly[methyl(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxyl)siloxane] **3** was prepared as follows: To a solution of TEMPO-OH (17.2 g, 100 mmol) in 100 mL of dry THF, $[\text{RhCl}(\text{cod})]_2$ (98 mg, 0.2 mmol; 0.25 mol%) and PMHS (5.0 g, 83.2 mmol) was added. The mixture was stirred at rt for 6 h. After the reaction, the resulting mixture was concentrated by rotary evaporation to leave a solvent. The crude product was washed with hexane (500 mL $\times$ 3) and Et_2O (500 mL $\times$ 3) to remove catalyst and excess TEMPO-OH. The residue was dried under reduced pressure to afford **3** (8.5 g, 36.9 mmol) as a red solid (44% yield). The polymer was pale red, which is attributable to

TEMPO radical. (IR-ATR) (Ge, cm^{-1}): 2975 ($\nu\text{C-H}$), 2943 ($\nu\text{C-H}$), 2919 (νCH_2), 1466, 1363, 1268, 1178, 1062, 1032 ($\nu\text{Si-O}$). Anal. Calcd For $(\text{C}_{10}\text{H}_{19}\text{NO}_3\text{Si})_n$: C, 52.4; H, 8.35; N, 6.11. Found: C, 45.4; H, 8.13; N, 4.71 (77.0% TEMPO-substituted). Since **3** was barely soluble in THF, CHCl_3 , and DMF, the molecular weight could not be estimated by SEC.

Fabrication of radical polymer/VGCF Composite Electrode

A radical polymer/VGCF composite electrode was fabricated by using the following method. First, radical polymer (200 mg) initially grounded beforehand by an automatic mortar was combined with VGCF (700 mg) as a conductive additive and PTFE (100 mg) as a binder, and this mixture was kneaded using a mortar. After about 10 min of kneading, the mixture was drawn out by using a roller to fabricate a thin, plate-shaped radical polymer/VGCF composite electrode (100 μm) (electrode composition: radical polymer 20 wt%, VGCF 70 wt%, and PTFE 10 wt%).

Cyclic Voltammetry

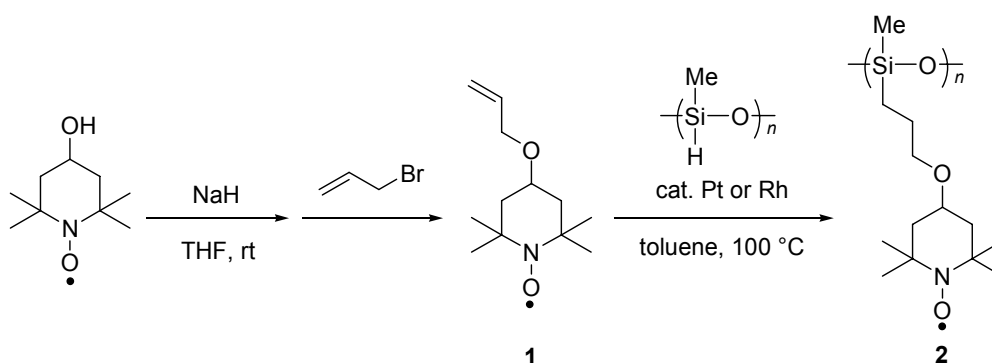
CV measurements using the fabricated radical **2**/VGCF composite electrode were performed in a voltage range of 3.0–4.2 V using 1 M LiPF_6 in EC/DEC (3:7 v/v) as the electrolyte, lithium metal as the reference electrode and counter electrode, and the **2**/VGCF composite electrode as the working electrode. The CV measurements were performed at a scan speed of $1 \text{ mV}\cdot\text{s}^{-1}$.

Fabrication of the Test Cell

Battery charge/discharge characteristics were evaluated by measurements performed on a coin-shaped cell (2320 type) at 25 °C. This coin-shaped cell was fabricated as follows. A disc 12 mm in diameter was punched out of a radical polymer/VGCF composite electrode (cathode) under vacuum was immersed in 1 M LiPF₆ in EC/DEC (3:7 v/v), which was then allowed to seep into voids on the electrode. The electrolyte-impregnated electrode was then overlaid with a polyolefin-porous film separator and lithium metal (anode) and placed within a stainless-steel package with insulation packing. The package was then closed by applying pressure.

2.3 Results and Discussion

Although hydrosilylation has been studied extensively³, the reaction of an unsaturated bond bearing a radical moiety has not been shown so far. We first examined the hydrosilylation of PMHS, which is commercially available poly(methylhydrosiloxane), with allyl ether of TEMPO for the introduction of the radical moiety into silicone backbone by employing the protocol of Hooper⁸ that is a hydrosilylation of allyl ethers without a radical moiety. We found that transition metal-catalyzed hydrosilylation occurred when PMHS and allyl ether **1**, which was prepared by the Williamson ether synthesis of TEMPO-OH and allyl bromide, was subjected to the reaction.



Scheme 1. Synthesis of TEMPO-substituted silicone **2**.

The allyl ether **1** was synthesized by a TEMPO-alkoxide, which was obtained by the reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO-OH) with sodium hydride, and allyl bromide. The formation of **1** was confirmed by measurement of the IR spectrum indicating the characteristic peak of C=C stretching at 1647 cm⁻¹ and disappearance of the broad peak of the OH group. Since measurement of NMR spectra

resulted in unsuccessful due to the paramagnetic characteristics derived by the nitroxyl radical, we transformed **1** into the corresponding *N*-hydroxyl compound by reduction with phenylhydrazine.

The hydrosilylation of PMHS with **1** in the presence of a platinum- or rhodium-catalyst took place and the corresponding hydrosilylated polymer **2** was obtained. IR spectrum measurements of the hydrosilylated polymers showed the peaks at 3081 cm^{-1} (H-C=) and 1647 cm^{-1} (C=C) and the peak at 2200 cm^{-1} (Si-H) observed in PMHS disappeared, demonstrating that the hydrosilylation proceeded sufficiently. However, the difference of the reactivity for the hydrosilylation of silicone with **1** was observed. When platinum complexes were used as a catalyst, both the yield and hydrosilylated ratio were higher than that of rhodium complexes. In particular, the reactivity of Karstedt's catalyst⁹ was found to be superior to any other catalyst and the hydrosilylated ratio of the polymer was estimated to be 76%. The lower reactivity of $[\text{Rh}(\text{cod})_2]\text{BF}_4$ was probably due to the low solubility of the catalyst in toluene. The ratio of hydrosilylation was estimated by elemental analysis of the obtained polymer. These results are summarized in Table 1.

Table 1. Hydrosilylation of a PMHS with allyl-O-TEMPO.^a

entry	cat.	C(%)	H(%)	N(%)	rate(%) ^b	yield(%)
1	K ₂ PtCl ₆	48.5	8.31	3.78	73.5	52
2	(Bu ₄ N) ₂ PtCl ₆	49.7	8.46	3.93	76.5	48
3	Karstedt's cat.	50.7	8.61	3.94	76.7	76
4	[RhCl(cod)] ₂	40.7	7.32	2.60	50.6	45
5	RhCl(PPh ₃) ₃	38.1	7.03	2.23	43.3	40
6	[RhCl(nbd)] ₂	30.4	6.07	1.40	27.2	34
7	[Rh(nbd) ₂]BF ₄	29.9	6.13	1.39	27.0	34
8	[Rh(cod) ₂]BF ₄	-	-	-	-	Trace
Calcd.		57.3	9.62	5.14	100	-

a) Unless otherwise noted, the reaction was performed with PMHS (10.4 mmol), catalydst (0.02 mmol; 0.2 mol%) and **1** (15.6 mmol) with 50 mL of the toluene at 100 °C. b) Hydrosilylated rate of **2** was estimated with elemental analysis.

On the other hand, characterization of the radical-substituted polymer **2** obtained by hydrosilylation with NMR and SEC was ineffective because it did not easily dissolve in an organic solvent.

The spin concentration of **2** was determined by measuring the ESR spectrum of powdered **2** ($g = 2.0076$). The g value was similar to those of PTMA^{5a} and PTV^{5c}. The spin concentration of **2**, which was synthesized with Karstedt's catalyst, was estimated to be 1.57×10^{21} spins·g⁻¹ (71% spin per repeating unit). The hydrosilylated ratio estimated by elemental analysis (76.7%) and the spin concentration estimated by ESR spectrum (71%) were approximately consistent. Although the Si-H bonds were completely disappeared, the spin concentration of **2** was lower than that of a theoretical value. These results suggest that radical deactivation or decrease occurred during the

hydrosilylation or purification processes.

We next investigated the electrochemical properties of **2** by performing CV measurements on a **2**/VGCF composite electrode. The results of these measurements are shown in Figure 1. Oxidation potential of 3.68 V (vs. Li/Li⁺) and reduction potential of 3.51 V (vs. Li/Li⁺) were observed, giving an estimated redox potential of 3.56 V (vs. Li/Li⁺). This redox potential is similar to those of PTMA^{5a} and PTVE^{5e} and is due to the oxidation of the nitroxide radical to the corresponding oxoammonium cation.

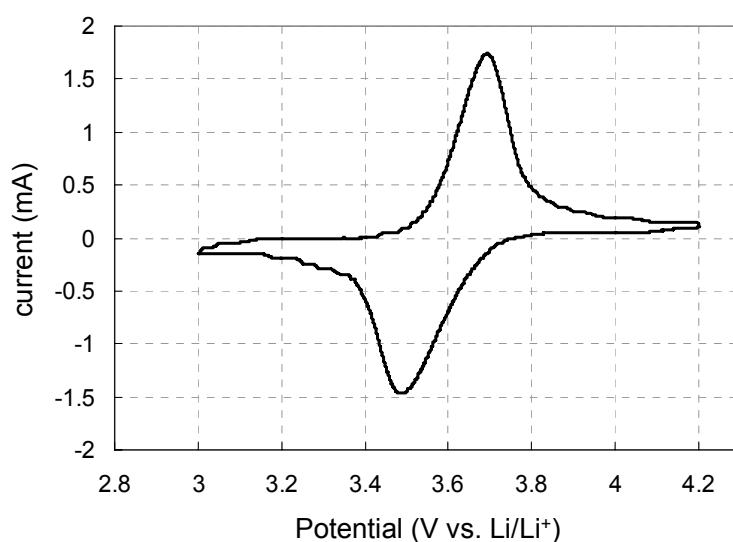


Figure 1. Cyclic voltammogram of a **2**/VGCF composite electrode with a **2** content of 20 wt%.

The initial charge/discharge curves with the coin-shaped cell, in which charge/discharge measurements were performed at a current density of 0.05 mA·cm⁻² (0.5 C) are shown in Figure 2. These curves show average voltages of 3.53 V for charging and 3.48 V for discharging, respectively, and show the discharge capacity of

46 mAh·g⁻¹, which is 47% of the theoretical capacity of **2** (98 mAh·g⁻¹).

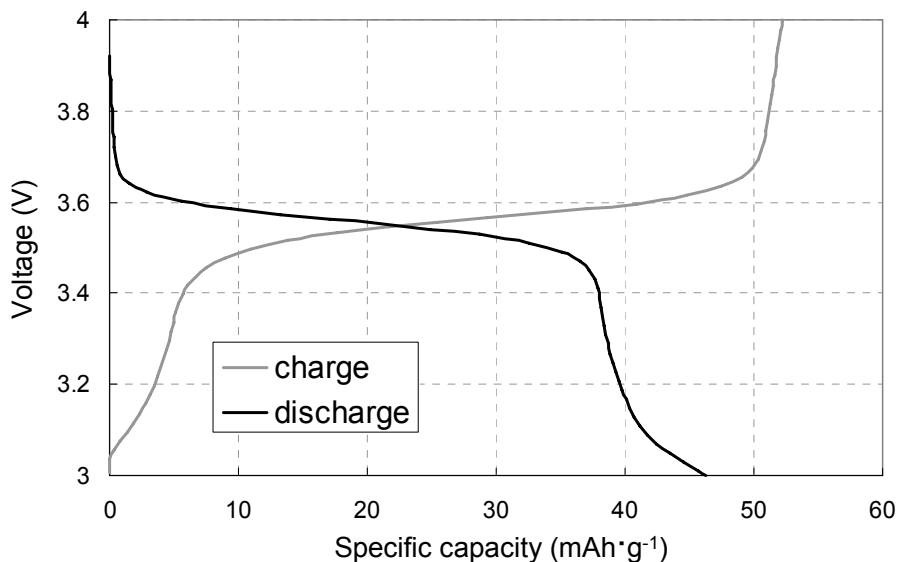
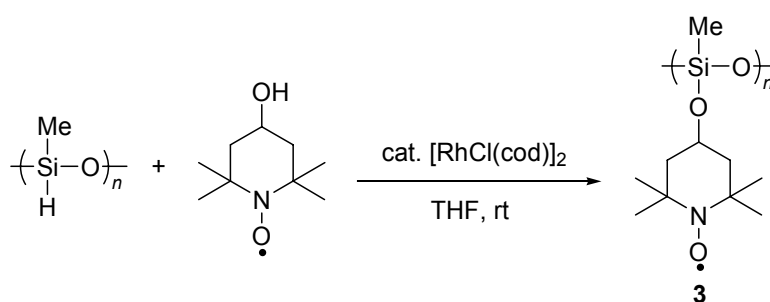


Figure 2. Charge/discharge curves for a Li/1 cell.

These electrochemical studies indicate that TEMPO-substituted silicone can be available as an active material for rechargeable batteries. However, the capacity of **2** is still lower because of the lower radical concentration toward the total mass of the polymer. Accordingly, we envisaged the synthesis of a new silicone-based radical polymer, which has an alkoxysilane bond of Si-O-TEMPO, in order to increase battery capacity toward the polymer mass. Synthesis of such alkoxysilane was carried out by rhodium-catalyzed dehydrogenative alcoholysis of silicone reported by Boudjouk,¹⁰ by which the reaction of PMHS with TEMPO-OH proceeded. A directly TEMPO-substituted silicone, poly[methyl(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-oxyl)siloxane] **3** was obtained by rhodium-catalyzed dehydrogenative alcoholysis of

PMHS with TEMPO-OH. The theoretical capacity of **3** ($116 \text{ mAh}\cdot\text{g}^{-1}$) is larger than that of not only silicone-based polymer **2** ($98 \text{ mAh}\cdot\text{g}^{-1}$) but also hydrocarbon-based polymer PTMA ($111 \text{ mAh}\cdot\text{g}^{-1}$). This is the first successful dehydrogenative alcoholysis of silicone with a radical moiety. The synthetic method for the directly TEMPO-substituted silicone **3** is shown in Scheme 2.



Scheme 2. Synthesis of the TEMPO-substituted silicone **3**.

The direct dehydrogenative alcoholysis of PMHS with TEMPO-OH was performed using 0.25 mol% of $[\text{RhCl}(\text{cod})]_2$ as a catalyst. The TEMPO-substituted ratio of **3**, which was estimated by elemental analysis, was 77.0% and the estimated capacity of **3** was found to be $89 \text{ mAh}\cdot\text{g}^{-1}$.

We also fabricated a coin-shaped cell using a **3**/VGCF composite electrode for the cathode and lithium metal for the anode, and then performed charge/discharge measurements at a current density of $0.05 \text{ mA}\cdot\text{cm}^{-2}$ (0.5 C) in a voltage range of 3.0-4.0 V. The initial charge/discharge curves obtained from these measurements are shown in Figure 3. These curves show an average voltage of 3.58 V for charging and 3.54 V for discharging and a discharge capacity of $80 \text{ mAh}\cdot\text{g}^{-1}$, which is 69% of the theoretical

capacity ($116 \text{ mAh}\cdot\text{g}^{-1}$) of **3**. The observed discharge capacity of **3** was found to be higher than that of **2**.

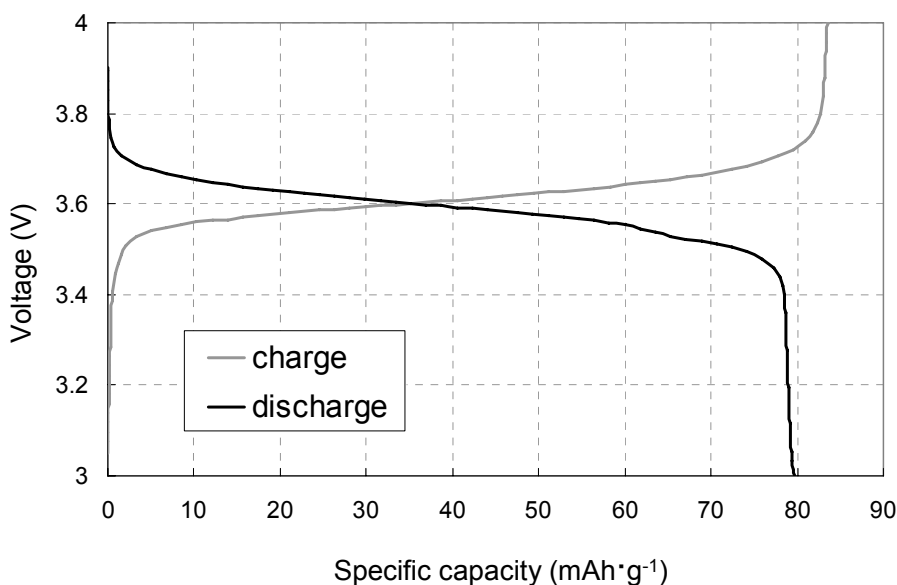


Figure 3. Charge/discharge curves for a Li/**3** cell

The long-term stability of rechargeable batteries is one of the most significant properties. We also investigated the cycling behavior of Li/**3** cell at $20\text{ }^{\circ}\text{C}$. The cycling behavior of Li/**3** cell is shown in Figure 4. The cycle was repeated at a constant current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ (1 C) within a voltage range of $3.0\text{--}4.0\text{ V}$. Interestingly, the initial discharge capacity of **3** remained after 100 cycles. The excellent cycling behavior of **3** can be explained by taking into consideration the high chemical stability of silicone backbone.

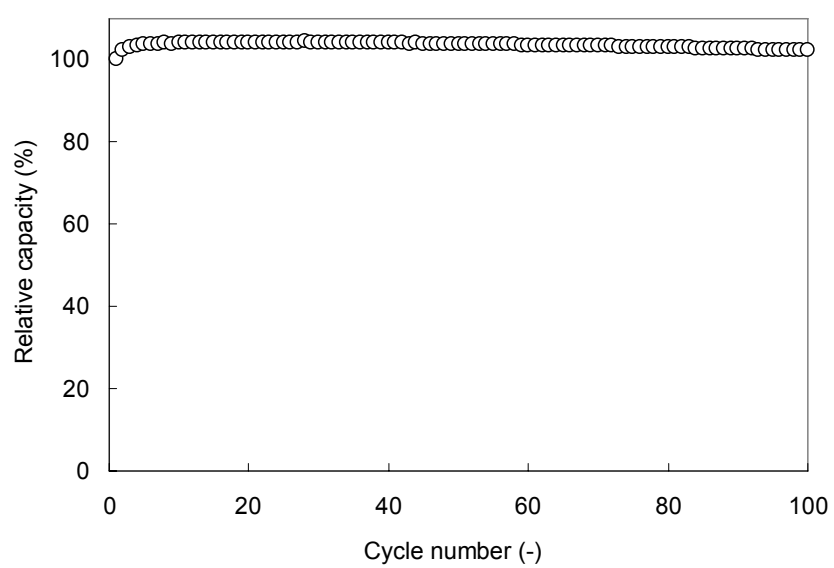


Figure 4 Cycling performance of Li/3 cell at 20 °C.

2.4 Conclusion

The two new silicone compounds bearing a TEMPO radical moiety were synthesized by platinum- or rhodium-catalyzed reactions of allyl-O-TEMPO or TEMPO-OH with PMHS. The use of LiCoO_2 , which is used as a cathode active material for lithium-ion batteries, is bounded by the cobalt resource. In contrast, the use of silicone compounds is not affected by the silicon resource since there is a large amount of silicon compounds on the earth. Silicone compounds are chemically stable and easily-obtainable. Furthermore, since silicone compounds have lower toxicity compared with transition metals, the use of silicone compounds as a cathode active material instead of transition metal oxide is environmentally friendly and sustainable. The observed charge-discharge properties of silicone indicate that silicone compounds are potentially practical as a next-generation active material for rechargeable batteries.

2.5 References and Notes

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Chapter 3

Cationic Polymerization of Poly(vinyl ether) bearing a TEMPO radical: A New Cathode Active Material for Organic Radical Batteries

Abstract: Poly(4-vinyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (PTVE), which contained the radical moiety, was synthesized as a new active material for organic radical batteries. Cationic polymerization of a monomer bearing a TEMPO radical moiety took place. The spin concentration of PTVE was estimated to be 2.75×10^{21} spins·g⁻¹ (100% spin/repeating unit). The PTVE is extremely stable—there is absolutely no decrease in spin concentration even when storing PTVE samples for more than a year under an aerobic condition at room temperature. The redox potential of PTVE was observed at 3.55 V (vs. Li/Li⁺) by CV measurements. A coin-shaped cell using a PTVE/VGCF composite electrode was also fabricated, and then performed charge/discharge measurements. The discharge capacity of PTVE was 114 mAh·g⁻¹ (84% of the theoretical value).

3.1 Introduction

Rechargeable batteries are used in portable electronic devices such as mobile telephones and laptop computers. However, use of LiCoO_2 , which is used as a cathode active material, in these batteries presents problems in terms of cost, toxicity, and thermal safety.¹

We first reported that organic radical polymers can be used as a cathode active material for Li-ion rechargeable batteries.² We recently synthesized a stable radical polymer, poly(4-methacryloyloxy-2,2,6,6-tetramethyl-piperidine-*N*-oxyl) (PTMA) bearing a TEMPO radical in its side chain, and used it as a cathode-active material. PTMA (theoretical capacity: $111 \text{ mAh}\cdot\text{g}^{-1}$) was synthesized by radical polymerization of a methacrylate monomer bearing an amino group and the subsequent radical formation of the polymer by successive oxidation.^{2,3} However, this indirect synthetic method was accompanied by incomplete oxidation of an amino group into a nitroxyl radical, resulting in insufficient radical concentration as charge-storage materials. Masuda et al. reported a direct synthetic method and battery properties of polynorbornene bearing a TEMPO radical moiety (theoretical capacity: $109 \text{ mAh}\cdot\text{g}^{-1}$).⁴ Although it is interesting that the polymerization enabled the use of a monomer bearing TEMPO radical moiety, the theoretical capacity as an active material was lower than that of PTMA.

In contrast, poly(vinyl ether) is one of the simplest structures of all general-purpose polymers. The simple structure of poly(vinyl ether) produces a much higher capacity (theoretical capacity: $135 \text{ mAh}\cdot\text{g}^{-1}$) than that of polymethacrylate (theoretical capacity of PTMA: $111 \text{ mAh}\cdot\text{g}^{-1}$)² or polynorbornene (theoretical capacity: $109 \text{ mAh}\cdot\text{g}^{-1}$).⁵ In this

paper, we herein report the direct cationic polymerization of a vinyl ether monomer bearing a TEMPO radical moiety. This is the first successful cationic polymerization of a radical monomer. We describe the fabrication of a PTVE/vapor grown carbon fiber (VGCF) composite electrode, the results of subjecting this electrode to cyclic voltammetry (CV) measurements, and the charge/discharge characteristics of a Li/PTVE coin-shaped cell.

3.2 Experimental Section

Materials

All organic synthesis reactions were performed under an argon atmosphere, and chemicals were purchased and used as-is unless otherwise noted. Vinyl acetate, sodium carbonate, dry toluene, and dry CH_2Cl_2 were all purchased from Wako Pure Chemical Inc. Boron-trifluoride-diethyl ether complex ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO-OH) were purchased from Tokyo Kasei Kogyo Co. Ltd. Chloro(1,5-cyclooctadiene)iridium (I) dimer ($[\text{IrCl}(\text{cod})]_2$) was synthesized from iridium (III) chloride trihydrate ($\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$) by a previously reported method.⁵ Polytetrafluoroethylene (PTFE) was purchased from DAIKIN Industries. Vapor grown carbon fibers (VGCFs) were purchased from Showa Denko.

General

IR measurements were performed using a Nicolet NEXUS 470 FT-IR spectrometer. Low-resolution mass spectrometry spectra were obtained using a Shimadzu GCMS-QP2010 spectrometer system. HRMS spectra were obtained using a JEOL JMS-700 micromass spectrometer system. Elemental analyses (EA) were recorded using EL and HERAEUS CHN-O RAPID elemental analyzers. ^1H and ^{13}C NMR spectra were measured using a Bruker ABANCE 400 spectrometer. Single crystal X-ray analysis was performed using a Rigaku RU-H2R diffractometer with graphite monochromated $\text{Cu-K}\alpha$ radiation and a rotating anode generator. ESR measurements were performed using a JEOL JES-FR30 spectrometer system. Spin concentration was computed from the absorption-area intensity obtained by double integration of a

first-order-derivative type of ESR spectrum. CV measurements were performed in a dry room (dew point ≤ -50 °C) using a CH Instruments CHI 604 electrochemical analyzer. The charge/discharge test was performed using a Keisokuki Center Battery Labo System, BLS5500 Series.

Monomer Synthesis

2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether **1** was prepared as follows: To a mixture of TEMPO-OH (25 g, 290.3 mmol), Na₂CO₃ (15.4 g, 145.1 mmol) and [IrCl(cod)]₂ (1.95 g, 2 mol%) in 250 mL of dry toluene, vinyl acetate (26.8 mL, 290.3 mmol) was added. The mixture was stirred at 90 °C for 5 h. The reaction mixture was concentrated with a rotary evaporator, and then added to 500 mL of hexane and stirred for 10 min. The mixture was passed through a Celite pad to remove any solid residue. The pad was washed with hexane. The combined filtrate was purified by flash chromatography on silica gel (hexane:ethyl acetate = 5:1) to afford the corresponding monomer as a red solid in 50% yield (14.5 g, 73 mmol). IR-ATR (Ge, cm⁻¹): 3115 (ν =C-H), 2990, 2976, 2943, 1634 (ν =C-H), 1462, 1379, 1202 (ν C-O-C), 1180, 1159, 1065 (ν C-O-C), 966 (ν =C-H). Measurement of an IR spectrum revealed that the broad peak derived from the OH group in TEMPO-OH had disappeared, while new peaks derived from the vinyl group appeared at 3115 cm⁻¹ (ν H-C=) and 1634 cm⁻¹ (ν C=C). Peaks at 1202 cm⁻¹ and 1065 cm⁻¹ derived from the ether bond (ν C-O-C) could also be observed, demonstrating that a vinyl ether monomer bearing a TEMPO radical was synthesized. HRMS *m/z* 198.2876 (calcd), 198.1492 (found). Anal. Calcd For

$C_{11}H_{20}NO_2$: C, 66.63; H, 10.17; N, 7.06. Found: C, 66.6; H, 9.9; N, 7.0. Since it is impossible to measure the ^1H and ^{13}C NMR spectra due to the free radical structure, we transformed **1** into a *N*-hydroxyl compound to measure the NMR spectra. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.14 (s, 6H, CH_3), 1.17 (s, 6H, CH_3), 1.48-1.54 (m, 2H, CH), 1.90-1.95 (m, 2H, CH), 3.99-4.01 (m, 1H, $H_2C=C$) 4.01-4.07 (m, 1H, $H_2C=COCH$), 4.26-4.30 (m, 1H, $H_2C=C$), 6.27-6.32 (m, 1H, $OCH=CH_2$), 6.77-6.79 (m, 1H, NOH). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 20.4 (CMe_2), 31.8 (CMe_2), 44.0 ($OCHCH_2$), 58.8 ($NCMe_2$), 70.4 ($H_2C=COCH$), 88.0 ($H_2C=CHO$), 162.9 ($H_2C=CHO$).

Polymer Synthesis

Poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE) was prepared as follows: To a solution of monomer **1** (10 g, 50.4 mmol) in 100 mL of dry CH_2Cl_2 , $BF_3 \cdot Et_2O$ (128 μ L, 1.01 mmol; 2 mol%) was added at -78 °C. The mixture was left to rest at -25 °C for 20 h. After the polymerization reaction, the resulting mixture changed to viscous reddish gel, which was washed with methanol to remove the initiator. The residue was dried under reduced pressure to afford PTVE as a red solid (70% yield). The obtained polymer was barely soluble in THF, chloroform ($CHCl_3$), DMF, and DMSO. PTVE's color was red, which is attributable to TEMPO radical. IR-ATR (Ge, cm^{-1}) 2974, 2938, 1464, 1362, 1244, 1177, 1067 ($\nu C-O-C$). Anal. Calcd For $(C_{11}H_{20}NO_2)_n$: C, 66.6; H, 10.1; N, 7.1. Found: C, 65.6; H, 9.9; N, 6.8. IR spectrum measurements revealed that the peaks at 3115 cm^{-1} ($\nu H-C=$) and 1634 cm^{-1} ($\nu C=C$) due to stretching vibrations of the vinyl group as observed in the monomer had disappeared,

demonstrating that the polymerization reaction had progressed sufficiently. Since PTVE was barely soluble in THF, CHCl_3 , and DMF, the molecular weight could not be estimated by SEC.

Fabrication of PTVE/VGCF composite electrode

A PTVE/VGCF composite electrode was fabricated by using the following method. First, PTVE (200 mg) initially grounded beforehand by an automatic mortar was combined with VGCF (700 mg) as a conductive additive and PTFE (100 mg) as a binder, and this mixture was kneaded using a mortar. After about 10 minutes of kneading, the mixture was drawn out by using a roller to fabricate a thin, plate-shaped PTVE/VGCF composite electrode (100 μm) (electrode composition: PTVE 20 wt%, VGCF 70 wt%, and PTFE 10 wt%).

Cyclic Voltammetry

CV measurements were performed using the fabricated PTVE/VGCF composite electrode (having a PTVE content of 20 wt%) in a voltage range of 3.0-4.2 V. In these measurements, ethylene carbonate (EC)/diethyl carbonate (DEC) (3:7 vol%), in which 1 mol/L of lithium hexafluorophosphate (LiPF_6) was dissolved, was used as an electrolyte. Lithium metal was used as a reference electrode and counter electrode, and the PTVE/VGCF composite electrode (having a PTVE content of 20 wt%) was used as a working electrode. The CV measurements were performed at a scan speed of $1 \text{ mV}\cdot\text{s}^{-1}$.

Fabrication of the batteries

Battery charge/discharge characteristics were evaluated by using measurements performed on a coin-shaped cell (2320 type) at 25 °C. This coin-shaped cell was fabricated by using the following method. First, a punched-out circular section of a PTVE/VGCF composite electrode (PTVE 20 wt%) with a diameter of 12 ϕ was immersed in an electrolyte, which was then allowed to seep into voids on the electrode within a vacuum. This PTVE/VGCF composite electrode impregnated with electrolyte was then overlaid with a polyolefin-porous film separator and lithium metal and placed within a stainless-steel package with insulation packing. Finally, the entire package was closed shut by applying pressure resulting in a coin-shaped cell for test purposes. A mixed solution of EC/DEC (3:7 vol%) with 1 mol/L of dissolved LiPF_6 was used here as the electrolyte.

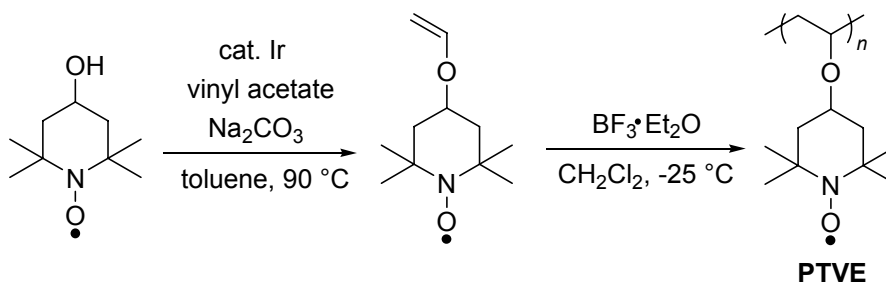
3.3 Results and Discussion

Monomer Synthesis

Although vinyl ethers are prepared by the reaction of acetylene with an alcohol, these synthetic methods are not plausible due to their severe reaction conditions or toxicity of the metal species used.⁶ We thereby envisaged easier synthesis of vinyl ethers and focused on the iridium-catalyzed transformation of vinyl acetate into vinyl alcohols, which was recently reported by Ishii.⁷ Their results indicated that the reaction was possible for an alcohol bearing a TEMPO radical moiety. The method for synthesizing the vinyl ether monomer bearing a TEMPO radical and the corresponding polymer are shown in Scheme 1. First, the monomer was synthesized by reacting vinyl acetate and TEMPO-OH in the presence of 2 mol% of $[\text{IrCl}(\text{cod})]_2$.

Polymer Synthesis

Although many studies for cationic polymerization of vinyl ether have been reported, cationic polymerization of vinyl ether bearing a radical moiety has not been reported. We found that cationic polymerization of a monomer bearing a TEMPO radical moiety took place. Direct polymerization of a radical monomer **1** was performed using 2 mol% of boron-trifluoride-diethyl ether complex ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) as a polymerization initiator.



Scheme 1. Synthesis of vinyl ether monomer bearing a TEMPO radical and corresponding polymer (PTVE)

The spin concentration of PTVE was determined by measuring the ESR spectrum of powdered PTVE. Figure 1 shows a spectrum obtained ($g = 2.0076$). The g value was almost similar to that obtained using PTMA.² As a result, the spin concentration of PTVE was estimated to be 2.75×10^{21} spins·g⁻¹ (100% spin/repeating unit). The results indicate that no radical deactivation or decrease in radical occurred during the purification protocols. The PTVE is extremely stable—there is absolutely no decrease in spin concentration even when storing PTVE samples for more than a year under aerobic conditions at room temperature. Although a considerable number of studies have been conducted on radical polymers,⁸ there have been no studies that tried to achieve both higher stability and higher spin concentration.

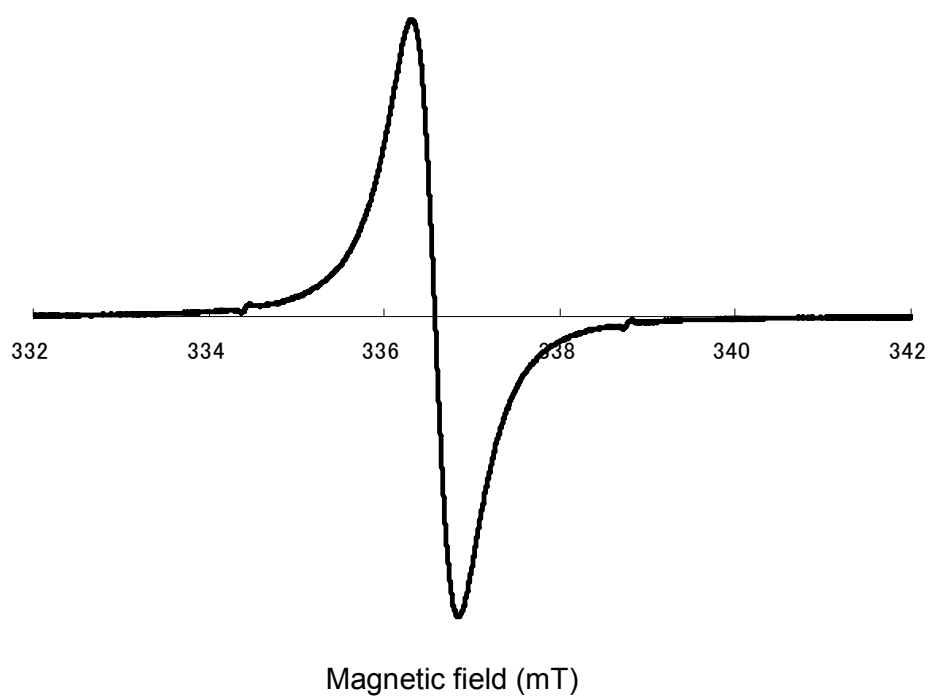


Figure 1. X-band ESR spectrum of PTVE at room temperature.

Electrochemical Properties of Polymer

We next investigated the electrochemical properties of PTVE by performing CV measurements on a PTVE/VGCF composite electrode. Figure 2 shows the results of these measurements. A PTVE oxidation potential and reduction potential of 3.62 V (vs. Li/Li^+) and 3.48 V (vs. Li/Li^+), respectively, were observed, giving an estimated redox potential of 3.55 V (vs. Li/Li^+).

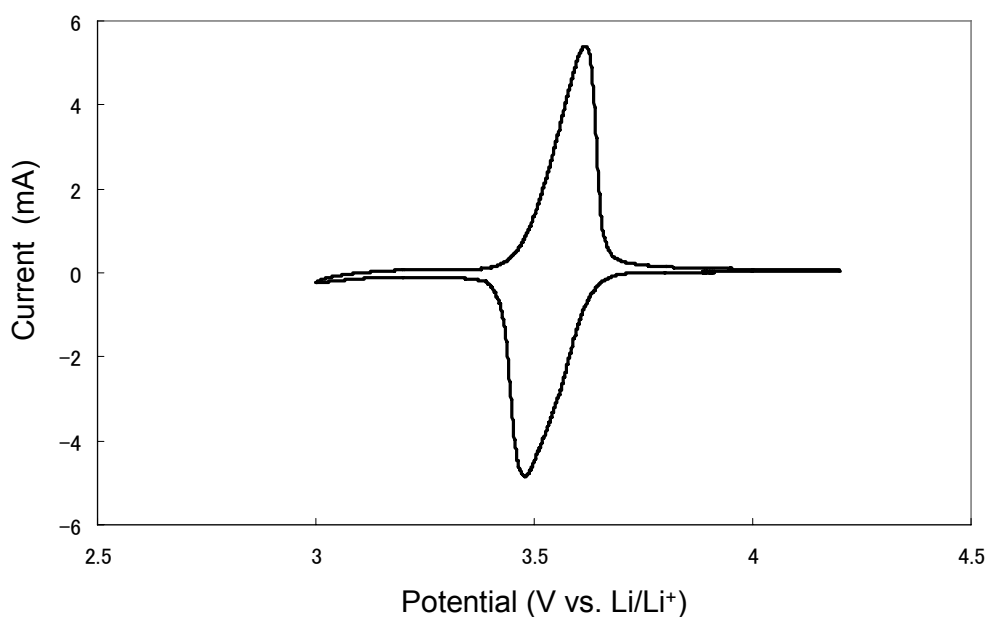


Figure 2. Cyclic voltammogram of a PTVE/VGCF composite electrode (having a PTVE content of 20 wt%) in a voltage range of 3.0-4.2 V.

We also fabricated a coin-shaped cell using a PTVE/VGCF composite electrode (100 μm) for the cathode and lithium metal for the anode, and then performed charge/discharge measurements at a current density of $0.09 \text{ mA}\cdot\text{cm}^{-2}$ (0.6 C) in a voltage range of 2.5-4.0 V. Figure 3 shows the initial charge/discharge curves obtained from these measurements. These curves show an average voltage of 3.55 V for charging and 3.51 V for discharging and a discharge capacity of $114 \text{ mAh}\cdot\text{g}^{-1}$. The discharge capacity obtained is 84% of the PTVE theoretical capacity ($135 \text{ mAh}\cdot\text{g}^{-1}$).

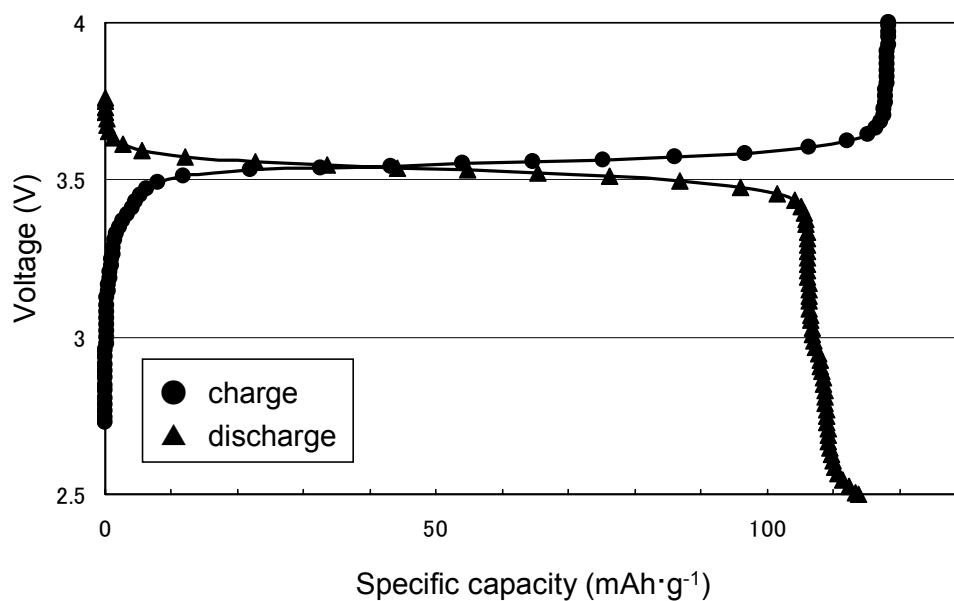


Figure 3. Charge/discharge curves for Li/PTVE battery at charge/discharge current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$.

In a previous paper, we reported the actual capacity of PTMA, which was obtained by the oxidation of amino group into nitroxyl radical, was $77 \text{ mAh}\cdot\text{g}^{-1}$.² It should be pointed out that the synthesized PTVE enabled the actual capacity of the battery to increase 150%, accordingly.

3.4 Conclusion

In conclusion, a vinyl ether polymer bearing TEMPO radical monomer and corresponding polymer (PTVE) were synthesized by using a direct synthetic method. Such a high spin concentration (2.75×10^{21} spins·g⁻¹) and a discharge capacity (114 mAh·g⁻¹) have not been achieved so far. The high capacity and excellent charge/discharge properties indicate that a wide range of potential applications of PTVE is expected as a new power source.

3.5 References and Notes

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Appendix

Crystallographic data and selected bond distances and angles

Table A-1. Crystallographic Data and Details of **1**

1	
Chemical formula	C ₁₁ H ₂₀ NO ₂
Formula wt	198.28
cryst system	triclinic
space group	<i>P</i> 1 (No.2)
<i>a</i> , Å	10.911(1)
<i>b</i> , Å	15.284(1)
<i>c</i> , Å	8.184(1)
α , deg	93.410(8)
β , deg	105.011(9)
γ , deg	107.832(6)
<i>V</i> , Å ³	1240.5(2)
<i>Z</i>	4
<i>D</i> _{calc} , g·cm ⁻³	1.062
μ , mm ⁻¹	5.76

Chapter 4

Effect of Ethylene Oxide Structures in TEMPO Polymers on High-Rate Discharge Properties

Abstract: A copolymerized poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE) was synthesized by cationic polymerization of a vinyl monomer bearing a TEMPO radical and an ethylene oxide or tri(ethylene oxide). The charge/discharge properties of copolymerized PTVE improved with the length of the ethylene oxide chain, and high-rate and high-power properties of the PTVE synthesized by copolymerization with tri(ethylene oxide) were much better than those of the PTVE homopolymer. Electrochemical measurements showed that the ionic conductivity of the polymer synthesized by copolymerization with tri(ethylene oxide) was higher than that of the PTVE homopolymer.

4.1 Introduction

LiCoO₂, which is used as a cathode active material in many of the lithium-ion rechargeable batteries in portable electronic devices such as mobile phones and laptop computers, presents thermal runaway, toxicity, and depletion problems.¹ Rechargeable batteries would be safer and more environmentally friendly if the cathode were an organic material rather than a transition metal oxide.² We have therefore been developing organic radical batteries (ORBs) in which stable organic radicals such as nitroxide radicals are used as the cathode active material for lithium-ion batteries. The active material used as the cathode in our first ORBs was an organic radical polymer poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (PTMA) bearing a 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical.³ We synthesized poly(4-vinyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) (PTVE) because its theoretical capacity (135 mAh·g⁻¹) is far higher than that of PTMA (111 mAh·g⁻¹) and because it produces increased energy density in ORBs.⁴

ORBs also have attracted much attention as a high power density and environmentally friendly rechargeable battery for a next-generation energy-storage device. The high charging and discharging rate performance resulting from the rapid electron-transfer processes of ORBs has been described.⁵ One of the current challenges in development of ORBs is enhancing the power density. We revealed that an Al-laminated film packaged battery using PTMA and packaged in an Al-laminated film might be suitable for high-power applications.⁶

On the other hand, a poly(ethylene oxide) (PEO) structure is well known as a high lithium-ion conductivity polymer⁷, and a number of PEO-based polymer electrolytes have been synthesized.⁸ We introduced an ethylene oxide chain into the PTVE structure in order to achieve a higher rate property and power density in the ORBs. The smooth ion conductivity and high power density of PTVE could be achieved by substitution with ethylene oxide. We herein report the high-rate and high-power discharge properties of coin-shaped cells in which the cathode is a composite made using vapor-grown carbon fiber (VGCF) and a copolymer of PTVE and either ethylene oxide or tri(ethylene oxide).

4.2 Experimental Section

General

Infrared (IR) absorption spectra were measured using a Nicolet NEXUS 470 FT-IR spectrometer, and high-resolution mass spectrometry (HRMS) spectra were obtained using a JEOL JMS-700 micromass spectrometer system. Elemental analyses (EA) were recorded using EL and HERAEUS CHN-O RAPID elemental analyzers. ^1H and ^{13}C NMR spectra were measured using a Bruker ABANCE 400 spectrometer. The thicknesses of the composite electrodes were measured using a Mitsutoyo ID-C112C thickness gauge, and the ion conductivities of PTVE and the PTVE copolymers were evaluated using a Solartron SI 1287 Electrochemical Interface and 1255B Frequency Response Analyzer. Charging and discharging were controlled using the BLS5500 Series Battery Labo System (Keisokuki Center Co.) and a Tabai Espec automatic battery measurement system. The charge/discharge measurements for the coin-shaped cell were made at 20 °C.

Materials

All organic reactions were performed under an argon atmosphere, and each chemical was purchased and used as-is unless otherwise noted. Vinyl acetate, sodium carbonate (Na_2CO_3), dry toluene, dry dichloromethane (CH_2Cl_2), hexane, ethyl acetate, methanol, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Kanto Chemical Co., Inc. Ethyleneglycolmethylvinyl ether and tri(ethyleneglycol)methylvinyl ether were donated

by Maruzen Petrochemical Co. Ltd. Boron-trifluoride-diethyl ether complex ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO-OH) were purchased from Tokyo Kasei Kogyo Co. Ltd. 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether (monomer **1**) was synthesized by iridium-catalyzed transvinilation. The synthesis method of **1** was described in Chapter 3. Polyvinylidene fluoride (PVdF) (KF#1710) was purchased from Kureha Corporation, and vapor-grown carbon fiber (VGCF) was purchased from Showa Denko K.K. Carboxymethylcellulose (CMC) was donated by Daicel Chemical Industries, Ltd. A microporous film separator (#2400) was donated by Celgard Inc. Ethylene carbonate (EC):diethyl carbonate (DEC) (3:7 vol%) mixtures containing $1 \text{ mol} \cdot \text{L}^{-1}$ lithium bis(pentafluoroethanesulfonyl)imide (LiBETI) or lithium hexafluorophosphate (LiPF_6) were purchased from Ube Industries Ltd.

Polymer synthesis

Poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE-homopolymer) was prepared as follows: A $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (191 μL , 1.5 mmol; 1.5 mol%) was added to a solution of monomer **1** (20 g, 100.8 mmol) in 200 mL of dry CH_2Cl_2 at -78°C , and the mixture was left at -25°C for 20 h to polymerize. The resulting mixture was a viscous reddish gel, which was washed with methanol to remove the initiator and then dried under reduced pressure to afford PTVE as a red solid (70% yield). IR-ATR (Ge, cm^{-1}) 2974, 2938, 1464, 1362, 1244, 1177, 1067 ($\nu_{\text{C-O-C}}$). Anal. calcd. for $(\text{C}_{11}\text{H}_{20}\text{NO}_2)_n$: C, 66.6; H, 10.1; N, 7.1. Found: C, 65.6; H, 9.9; N, 6.8. The polymer's molecular weight

could not be estimated by size exclusion chromatography (SEC) with THF, CHCl₃, or DMF because PTVE is barely soluble in any of these solvents.

PTVE-(ethylene oxide) copolymer was prepared as follows: A BF₃·Et₂O (191 μL, 1.5 mmol; 1.5 mol%) was added to a solution of monomer **1** (20 g, 100.8 mmol) and ethyleneglycolmethylvinyl ether (206 mg, 2 mmol) in 200 mL of dry CH₂Cl₂ at -78 °C, and the mixture was left at -25 °C for 20 h. After the polymerization reaction, the resulting mixture changed to viscous reddish gel, which was washed with methanol to remove the initiator. The residue was dried under reduced pressure to afford PTVE as a red solid (84% yield). IR-ATR (Ge, cm⁻¹) 2973, 2936, 1462, 1376, 1362, 1243, 1177, 1065 (νC-O-C). Anal. calcd. for (C₁₁H₂₀NO₂)_n: C, 65.48; H, 10.16; N, 6.92. Found: C, 65.6; H, 10.2; N, 6.6. The polymer's molecular weight could not be estimated by SEC with THF, CHCl₃, or DMF because PTVE-(ethylene oxide) is barely soluble in any of these solvents.

PTVE-tri(ethylene oxide) copolymer was prepared as follows: A BF₃·Et₂O (191 μL, 1.5 mmol; 1.5 mol%) was added to a solution of monomer **1** (20 g, 100.8 mmol) and tri(ethyleneglycol)methylvinyl ether (384 mg, 2 mmol) in 200 mL of dry CH₂Cl₂ at -78 °C, and the mixture was left at -25 °C for 20 h. After the polymerization reaction, the resulting mixture changed to viscous reddish gel, which was washed with methanol to remove the initiator. The residue was dried under reduced pressure to afford PTVE as a red solid (80% yield). IR-ATR (Ge, cm⁻¹) 2973, 2936, 1376, 1362, 1177, 1065 (νC-O-C). Anal. calcd. for (C₁₁H₂₀NO₂)_n: C, 66.44; H, 10.16; N, 6.92. Found: C, 65.5; H, 10.2; N, 6.6. The polymer's molecular weight could not be estimated by SEC with

THF, CHCl_3 , or DMF because PTVE-tri(ethylene oxide) is barely soluble in any of these solvents.

Fabrication of PTVE-VGCF composite electrode

The PTVE cathode was prepared using the following procedure. After 1.5 g of PVdF was dissolved in 50 g of NMP, 0.5 g of PTVE and 3.0 g of VGCF were added and the solution was stirred intensively. The resulting slurry was spread on aluminum foil using the doctor blade method. After the NMP was evaporated by heating ($120\text{ }^\circ\text{C}$, 10 min), the cathode was dried under a high vacuum at $60\text{ }^\circ\text{C}$ for 20 h. The composite layer was $100\text{ }\mu\text{m}$ thick and contained 10 wt% PTVE, 60 wt% VGCF, and 30 wt% PVdF.

The fabrication of the cathodes with the PTVE-(ethylene oxide) and PTVE-tri(ethylene oxide) copolymers were carried out in a manner to that of PTVE.

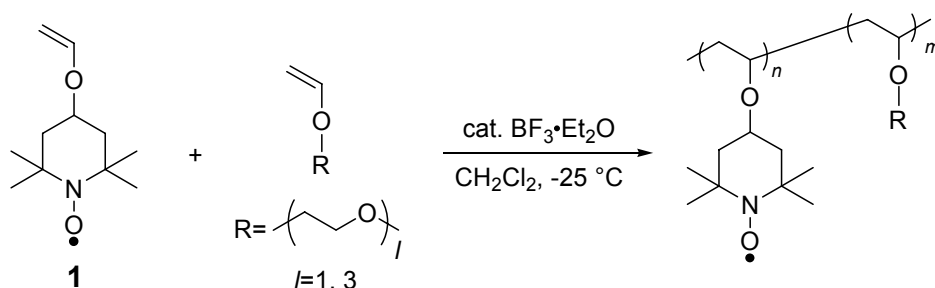
Fabrication of coin-shaped cells

Coin-shaped cells (2320 type) for test purposes were fabricated using the following method. First, a punched-out circular section of a PTVE-VGCF composite electrode containing 10 wt% of either PTVE, PTVE-(ethylene oxide), or PTVE-tri(ethylene oxide) that was 12 mm in diameter. The electrode was immersed in EC/DEC containing $1\text{ mol}\cdot\text{L}^{-1}$ LiBETI and was then allowed to seep into voids on the electrode. The electrolyte-impregnated composite electrode was then overlaid with a polyolefin porous-film separator (Celgard #2400) and a lithium disk 1.4 mm thick and was placed

within a stainless-steel package with insulation packaging. Finally, pressure was applied to form the package into a coin-shaped cell.

4.3 Results and Discussion

The modified PTVE was synthesized by copolymerization of a vinyl ether monomer bearing a TEMPO radical and one bearing an ethylene oxide chain. The synthetic route of PTVE-homopolymer and copolymer is shown in Scheme 1. Copolymerization of monomer **1** and an (ethylene oxide)-substituted vinyl ether was carried out in CH_2Cl_2 for 20 h with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a polymerization initiator.



Scheme 1. Synthetic route of PTVE-(ethylene oxide) or PTVE-tri(ethylene oxide) copolymers. Unless otherwise noted, the polymerization was carried out using 100.8 mmol of **1**, 2 mmol (2 mol%) of ethyleneglycolmethylvinyl ether or tri(ethyleneglycol)methylvinyl ether, and 1.5 mmol (1.5 mol%) of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at -25°C in 200 mL of dry CH_2Cl_2 .

Measurement of ion conductivity

The ion conductivity of gels that contained from 5 to 20 wt% of either PTVE-homopolymer or PTVE-tri(ethylene oxide) and $1 \text{ mol} \cdot \text{L}^{-1}$ LiPF_6 in EC/DEC=3/7 (3:7 vol%) was estimated from AC impedance measurements. As shown in Figure 1, the

ion conductivity depended on the amount of organic solvent. The ion conductivity of PTVE-tri(ethylene oxide), $5.2 \text{ mS}\cdot\text{cm}^{-1}$, was greater than that of PTVE-homopolymer, $4.2 \text{ mS}\cdot\text{cm}^{-1}$. PTVE-homopolymer has an extremely condensed structure and inhibits smooth ion transport because of the TEMPO radical, which has high steric hindrance²³, in all monomer units. These results indicate that the tri(ethylene oxide) chain, which has high flexibility, high ion conductivity, and low steric hinderance, provided PTVE with smooth ionic transport.

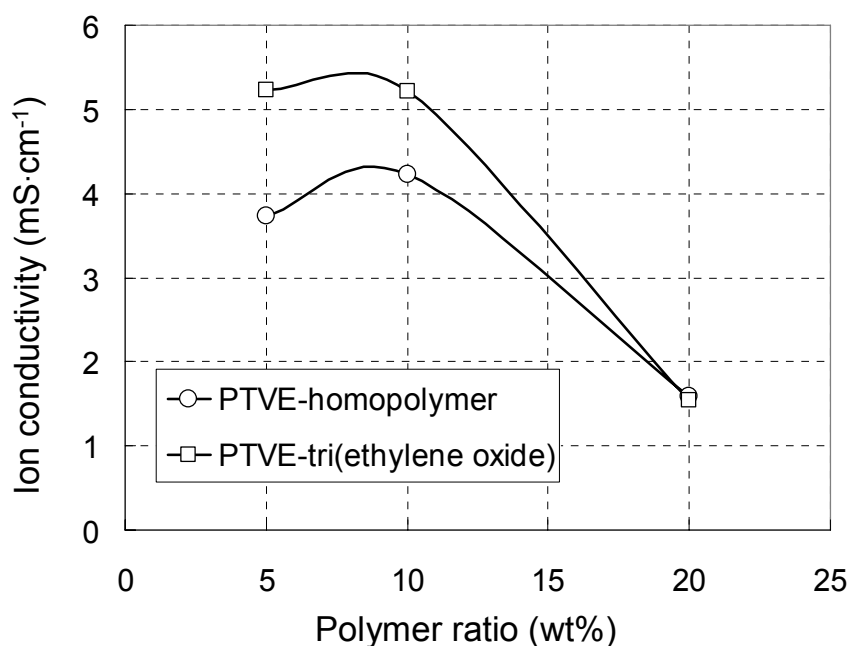


Figure 1. Ion conductivity of PTVE-homopolymer and PTVE-tri(ethylene oxide) gels at 20 °C. The ion conductivity of gels that contained from 5 to 20 wt% of either PTVE-homopolymer or PTVE-tri(ethylene oxide) and $1 \text{ mol}\cdot\text{L}^{-1}$ LiPF_6 in $\text{EC}/\text{DEC}=3/7$ (3:7 vol%) was estimated by AC impedance measurements.

Charge/discharge properties

The first charge and discharge curves for the coin-shaped cell using the composite cathode consisting of VGCF and PTVE-(ethylene oxide) or PTVE-tri(ethylene oxide) at 20 °C are shown in Figure 2. The charging and discharging was carried out at a constant current density of $0.2 \text{ mA}\cdot\text{cm}^{-2}$ (1 C) in the voltage range of 3.0-4.0 V. A plateau is apparent in both the charge and discharge processes. The average discharge voltage was 3.55 V. The first discharge capacity of a half-cell with a composite electrode containing PTVE-(ethylene oxide) was $103 \text{ mAh}\cdot\text{g}^{-1}$. Since the theoretical capacity of PTVE is $135 \text{ mAh}\cdot\text{g}^{-1}$, 77% of the radicals contributed to a one-electron reaction. The capacity of the half-cell with a cathode containing PTVE-tri(ethylene oxide) was $113 \text{ mAh}\cdot\text{g}^{-1}$, which is higher than that of one with a cathode containing PTVE-(ethylene oxide). This higher efficiency of PTVE-tri(ethylene oxide) is also due to smooth ionic transport.

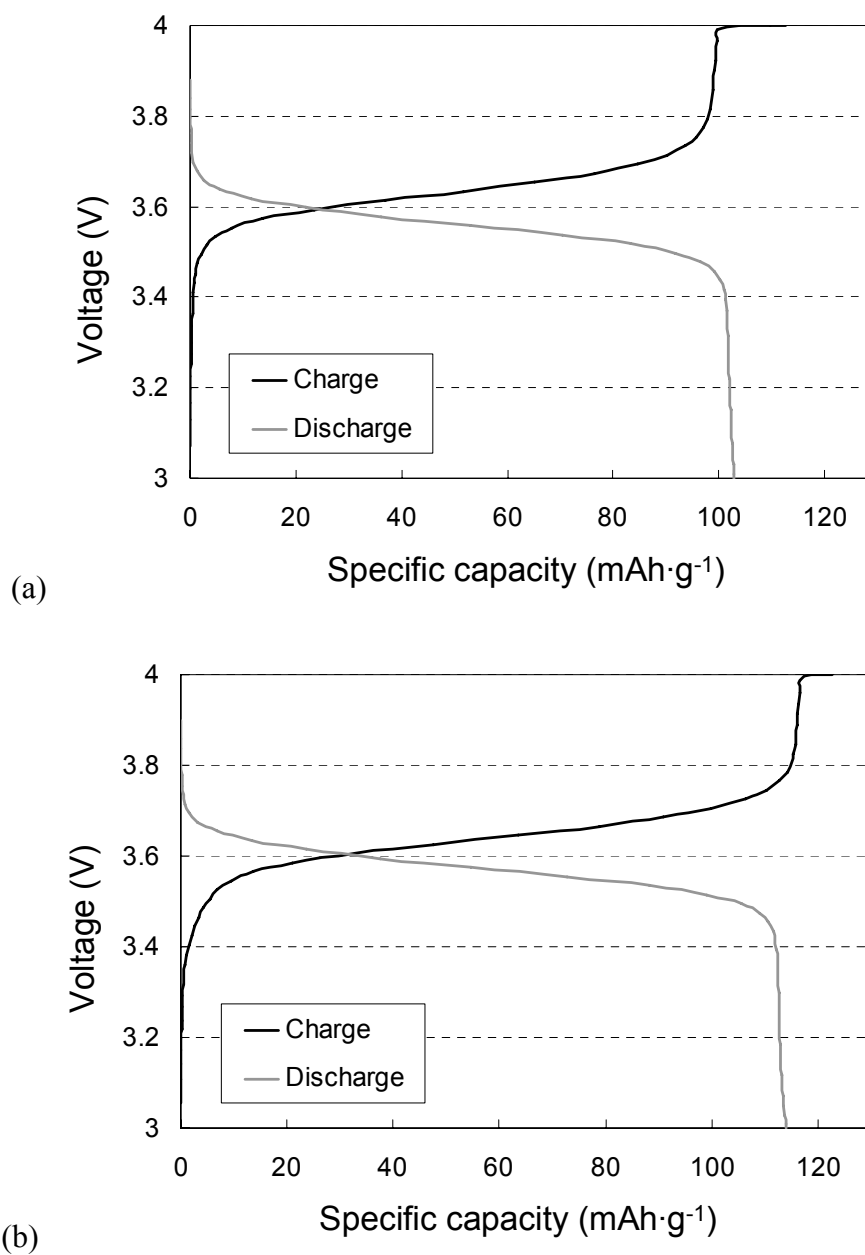


Figure 2. First charge/discharge curves for coin-shaped cells with PTVE cathode and lithium metal anode at 20 °C: (a) PTVE-ethylene oxide; (b) PTVE-tri(ethylene oxide). EC:DEC (3:7 vol%) mixtures containing 1 mol·L⁻¹ LiBETI was used as an electrolyte. The charging and discharging was carried out at a constant current density of 0.2 mA·cm⁻² (1 C) in the voltage range of 3.0-4.0 V.

High-rate capability

The specific capacities of coin-shaped cells with composite cathodes were measured at various discharge rates from 1 C to 20 C. The high-rate discharge properties are shown in Figure 3. When the cells were discharged at 20 C, the cells containing PTVE-homopolymer and PTVE-(ethylene oxide) showed specific capacities of only 80 and 75 mAh·g⁻¹, respectively. In contrast, the cell with the PTVE-tri(ethylene oxide) showed a specific capacity of 97 mAh·g⁻¹, which is 85% of the capacity at 1 C (114 mAh·g⁻¹). Thus, we found that the high-rate discharge properties of PTVE were markedly improved by copolymerization with tri(ethylene oxide). Because the ionic transport properties of PTVE gels were enhanced by copolymerization, the high-rate discharge properties were improved.

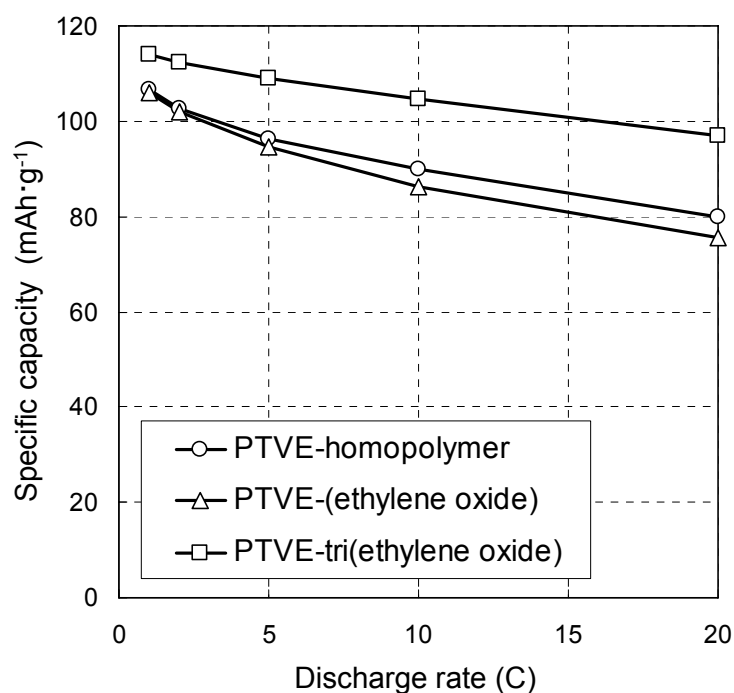


Figure 3. Relationship between discharge rate and specific capacities of coin-shaped cells containing various modified-PTVE cathode and lithium metal anode at 20 °C. EC:DEC (3:7 vol%) mixtures containing 1 mol·L⁻¹ LiBETI was used as an electrolyte. Charging current was 0.2 mA/cm⁻² (1 C).

High-power properties

We also measured high-power properties of PTVE. The relationship between the cell voltage and the current density is shown in Fig. 4(a). When the PTVE-homopolymer was used as a cathode active material, the cell voltage markedly dropped at current densities over 50 mA·cm⁻². In contrast, the cell voltage of PTVE-ethylene oxide and PTVE-tri(ethylene oxide) is higher than that of PTVE-homopolymer. These results

demonstrate that the ethylene oxide chain restrains the cell voltage drop. The effects depend on the length of the ethylene oxide chain.

The relationship between the power density and current density is shown in Fig. 4(b). While the power density of PTVE-homopolymer was found to be $116 \text{ mW}\cdot\text{cm}^{-2}$ at $50 \text{ mA}\cdot\text{cm}^{-2}$, PTVE-(ethylene oxide) afforded a power density of $130 \text{ mW}\cdot\text{cm}^{-2}$ at $60 \text{ mA}\cdot\text{cm}^{-2}$. Furthermore, PTVE-tri(ethylene oxide) showed a much higher power density of $139 \text{ mW}\cdot\text{cm}^{-2}$ at $70 \text{ mA}\cdot\text{cm}^{-2}$. This advantage of PTVE-tri(ethylene oxide) was in reasonable agreement with the ion conductivities. The rapid voltage drop in PTVE-homopolymer over $50 \text{ mA}\cdot\text{cm}^{-2}$ can be explained by the shortage of counter anions (PF_6^-) during high-power discharge. These high-power properties demonstrate that the tri(ethylene oxide) chain plays an important role in increasing the power density of PTVE.

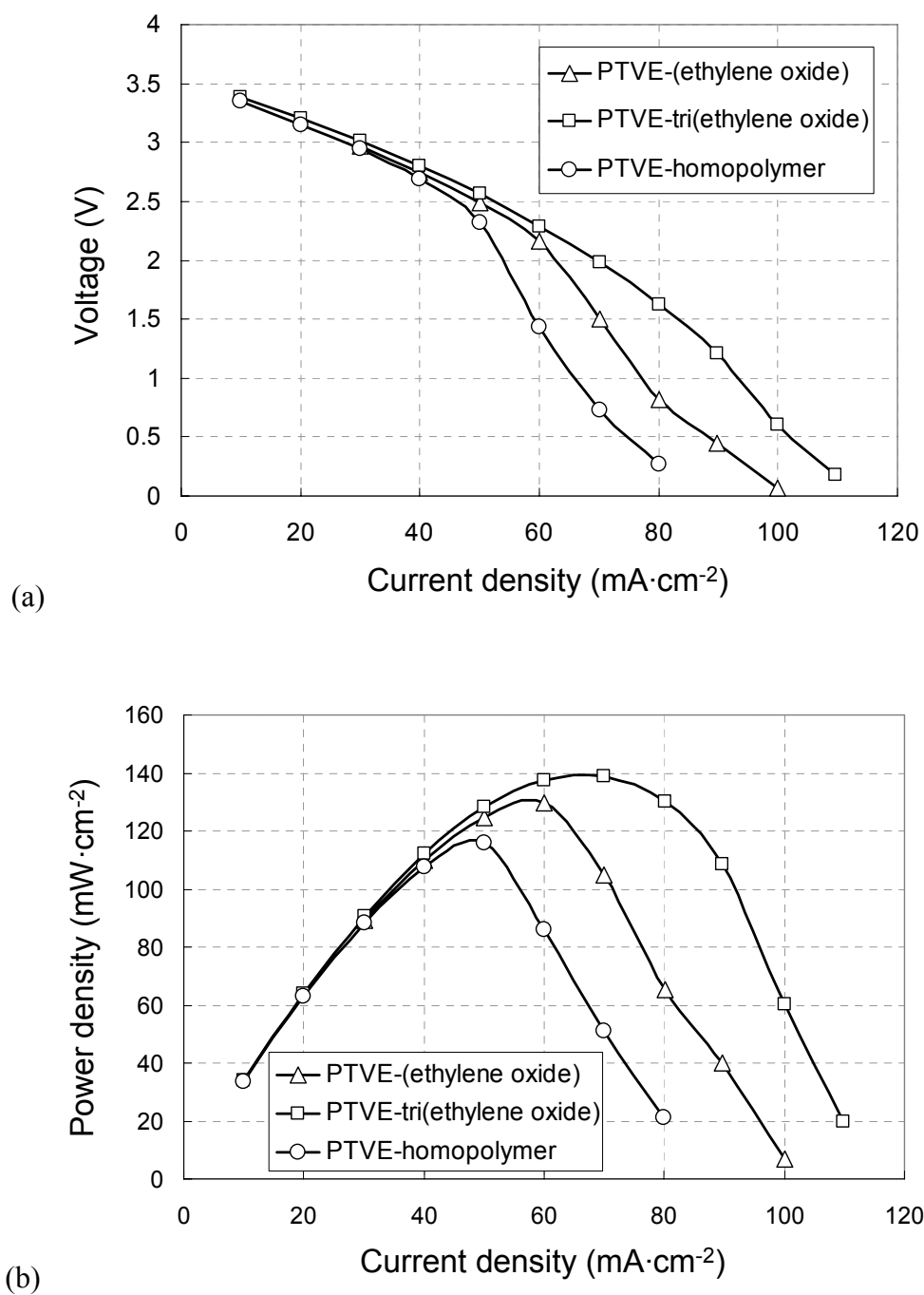


Figure 4. Relationship between discharge current density and (a) cell voltage and (b) power density after 1 second discharge at various current densities. EC:DEC (3:7 vol%) mixtures containing $1\text{ mol}\cdot\text{L}^{-1}$ LiPF_6 was used as an electrolyte. Charging current was 0.2 mA (1 C).

4.4 Conclusion

We synthesized PTVE polymers modified with ethylene oxide or tri(ethylene oxide). Investigating the charge/discharge characteristics of a Li/(copolymerized PTVE) coin-shaped cell, we found the high-rate and high-power properties to be improved when the PTVE was copolymerized with tri(ethylene oxide). Utilization of organic compounds as a cathode active material for rechargeable batteries is safer, transition metal free, and, environmentally friendly. The excellent high-rate and high-power properties of modified PTVE indicate that it will have a wide range of potential applications in new power sources.

4.5 References and Notes

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Chapter 5

Fabrication of a Practical and Polymer-Rich Organic Radical Polymer Electrode and its Rate Dependence

Abstract: A practical and polymer-rich organic radical cathode, which contains 80 wt% PTVE and 15 wt% VGCF, was fabricated. The PTVE/VGCF composite electrode showed a reversible redox peak at 3.56 V (vs Li/Li⁺) in CV. A coin-shaped cell with the PTVE/VGCF composite electrode as the cathode and lithium metal as the anode was also fabricated and was used for charge/discharge measurements. When the cell was discharged at 0.3 mA·cm⁻² (1 C), the capacity of 104 mAh·g⁻¹, which is 77% of PTVE's theoretical capacity (135 mAh·g⁻¹), was obtained. When it was discharged at 9.0 mA·cm⁻² (30 C), its capacity was 52% of the capacity it had when it was discharged at 0.3 mA·cm⁻² (1 C). Even when discharged at 24 mA·cm⁻² (80 C), it surprisingly had 32% of the capacity it had when discharged at 0.3 mA·cm⁻². The observed rate dependence shows that the polymer-rich electrode could discharge over 50% of the cell capacity in two minutes and over 30% within one minute.

5.1 Introduction

Rechargeable batteries are widely used in portable electronic devices such as mobile telephones and laptop computers. However, the LiCoO_2 used as their cathode active material presents problems in terms of toxicity and thermal safety.¹ An organic material rather than a transition metal oxide as the cathode active material of rechargeable batteries makes them more environmentally friendly and safer.² We previously reported that organic radical polymer, such as PTMA, which has a TEMPO radical moiety, have potential for use as an environmentally friendly cathode active material (theoretical capacity: $111 \text{ mAh}\cdot\text{g}^{-1}$) for Li-ion rechargeable batteries.³ We very recently synthesized PTVE as a high-capacity active material (theoretical capacity: $135 \text{ mAh}\cdot\text{g}^{-1}$)⁴ and reported the fundamental battery properties of a coin-shaped cell with PTVE as the active material in its cathode. However, the cathode contained only 20 wt.-% PTVE as an active material and 70 wt% carbon as an electron-conductive material. Since the cell capacity significantly depends on the amount of active materials in the electrode, we have fabricated a far more polymer-rich electrode. In this paper, we herein report the fabrication of a practical and polymer-rich PTVE/VGCF⁵ composite electrode containing 80 wt% PTVE, the results of subjecting this electrode to CV measurements, and the high-rate charge/discharge characteristics of the Li/PTVE coin-shaped cell.

5.2 Experimental Part

General

IR absorption spectrum measurements were performed using a Nicolet NEXUS 470 FT-IR spectrometer. HRMS spectra were obtained using a JEOL JMS-700 micromass spectrometer system. Elemental analyses (EA) were recorded using EL and HERAEUS CHN-O RAPID elemental analyzers. ^1H and ^{13}C NMR spectra were measured using a Bruker ABANCE 400 spectrometer. The thickness of the composite electrode was measured using a Mitsutoyo ID-C112C thickness gauge. The electrode surfaces were observed using a Keyence VE-9800 scanning electron microscope. CV measurements were performed in a dry room (dew point $\leq -50\text{ }^{\circ}\text{C}$) using a CH Instruments CHI 604 electrochemical analyzer. CV measurements of the PTVE/VGCF composite electrode were performed in a voltage range of 2.5–4.5 V at a scan speed of $1\text{ mV}\cdot\text{s}^{-1}$. The reference electrode was lithium, the counter electrode was lithium, and the PTVE/VGCF composite electrode was used as the working electrode. The electrolyte was $1.0\text{ mol}\cdot\text{L}^{-1}\text{ LiPF}_6$ in propylene carbonate. Charging and discharging were controlled using the BLS5500 Series Battery Labo System (Keisokuki Center Co.) and a Tabai Espec automatic battery measurement system. The charge/discharge measurements for the coin-shaped cell were performed at $25\text{ }^{\circ}\text{C}$.

Materials

All organic reactions were performed under an argon atmosphere, and each chemical was purchased and used as-is unless otherwise noted. Vinyl acetate, sodium carbonate

(Na₂CO₃), dry toluene, dry dichloromethane (CH₂Cl₂), hexane, ethyl acetate, methanol, and NMP were all purchased from Kanto Chemical Co., Inc. Boron-trifluoride-diethyl ether complex (BF₃·Et₂O) and TEMPO-OH were purchased from Tokyo Kasei Kogyo Co. Ltd. 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether (monomer **1**) was synthesized by iridium-catalyzed transvinylation. The synthesis method of **1** was described in Chapter 3. PTFE was purchased from Daikin Industries, Ltd. VGCF was purchased from Showa Denko K.K. CMC was donated by Daicel Chemical Industries, Ltd. Microporous film separator (#2400) were donated by Celgard Inc. All electrolytes were purchased from Ube Industries Ltd.

Polymer Synthesis

Poly(2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-vinyl ether) (PTVE) was prepared as follows: To a solution of monomer **1** (10 g, 50.4 mmol) in 100 mL of dry CH₂Cl₂, BF₃·Et₂O (128 μL, 1.01 mmol; 2 mol%) was added at -78 °C. The mixture was left to rest at -25 °C for 20 h. After the polymerization reaction, the resulting mixture changed to viscous reddish gel, which was washed with methanol to remove the initiator. The residue was dried under reduced pressure to afford PTVE as a red solid (70% yield). IR-ATR (Ge, cm⁻¹) 2974, 2938, 1464, 1362, 1244, 1177, 1067(ν_{C-O-C}). Anal. Calcd For (C₁₁H₂₀NO₂)_n: C, 66.6; H, 10.1; N, 7.1. Found: C, 65.6; H, 9.9; N, 6.8. Since PTVE was barely soluble in THF, CHCl₃, and DMF, the molecular weight could not be estimated by size exclusion chromatography (SEC).

Fabrication of Polymer/VGCF Composite Electrode

To 42 g of water, 400 mg of CMC (1380, Daicel Corp.) was added, and stirred until it was dissolved completely. Then 100 mg of PTFE fine powder (60 wt% water dispersion, D-1B), 8.0 g of PTVE, and 1.5 g of VGCF were added to the CMC solution and stirred intensively for 1 h. The resulting slurry was spread on aluminum foil by the doctor blade method on one side and then the solvent water was evaporated by heating (50 °C, 10 min). This electrode was dried under a high vacuum at room temperature. The composite layer was 100 μm thick and contained 80 wt% PTVE, 15 wt% VGCF, 4 wt% CMC, and 1 wt% PTFE.

Fabrication of Coin-Shaped Cell

This coin-shaped cell (2320 type) was fabricated by the following method. First, a punched-out circular section of a PTVE/VGCF composite electrode (PTVE 80 wt%) with a diameter of 12 ϕ was immersed in an electrolyte, which was then allowed to seep into voids on the electrode within vacuum. This PTVE/VGCF composite electrode impregnated with electrolyte was then overlaid with a polyolefin-porous film separator (Celgard #2400) and lithium disk (1.4 mm thick) and placed within a stainless-steel package with insulation packing. Finally, pressure was applied to form the package into a coin-shaped cell for test purposes. A mixed solution of EC/DEC (3:7 vol%) with 1 $\text{mol}\cdot\text{L}^{-1}$ of dissolved LiPF_6 was used here as the electrolyte.

5.3 Results and Discussion

Fabrication of the Electrode and its SEM Observation

In previous chapter, the Author fabricated a 20 wt% PTVE electrode⁴, which was fabricated by kneading the mixture of polymer, carbon, and PTFE binder. However, the electrode was not practical because the capacity and content percentage of the active material were lower than that of conventional electrodes. Besides, the electrode was extremely fragile because it was a naked polymer/carbon composite and was not fabricated on aluminum collector. Since the high-capacity and adequate strength were not obtained in the 20 wt% PTVE electrode, we attempted to fabricate a practical polymer/carbon composite electrode.

Since NMP has been used as a solvent for the electrode fabrication process of conventional lithium-ion secondary batteries⁷, we attempted to use NMP for the PTVE/VGCF composite electrode fabrication process. However, the NMP-based slurry afforded a cracked and curved electrode after solvent drying. The rough electrode indicated that PTVE swelled too much upon exposure to NMP. We therefore decided to try water as a slurry solvent for the PTVE/VGCF composite electrode fabrication process since water does not cause PTVE polymer to swell. We found that a practical and polymer-rich electrode containing 80 wt% PTVE could be fabricated by means of the water-based slurry process. Since the 80 wt% PTVE electrode was fabricated on aluminum collector, the strength of the electrode is sufficient for battery use. Hence, the 80 wt% PTVE electrode can be easily handled compared with 20 wt% one.

A SEM image of a PTVE/VGCF composite electrode containing 80 wt% PTVE is shown in Figure 1. Although the amount of VGCF (15 wt%) in contained the electrode is lower than that of PTVE (80 wt%), this SEM image shows that VGCF was dispersed as an encircling network on the surface of PTVE particles with diameters ranging from several to a few ten micrometers. These results would be explained in terms of the low bulk density and long fiber length of VGCF.⁵ Although we also fabricated PTVE/carbon composite electrodes using other carbon sources (e.g. ketjen black and acetylene black)⁸ as an electron-conductive material, a lot of cracks were observed in the PTVE/carbon composite electrodes and flat electrodes were not fabricated. These results indicate that VGCF plays an important role in reinforcing of polymer/carbon composite electrodes.⁹ This advantage of VGCF, which is attributable to its fabric construction, is not attainable in the carbon materials commonly used as electron-conductive materials⁸ in lithium-ion batteries. Since VGCF has a long fiber length compared with other carbon materials and can be closely contacted with not only adjacent PTVE but also adjacent VGCF, the electron transfer of PTVE/VGCF composite electrode would be smooth.

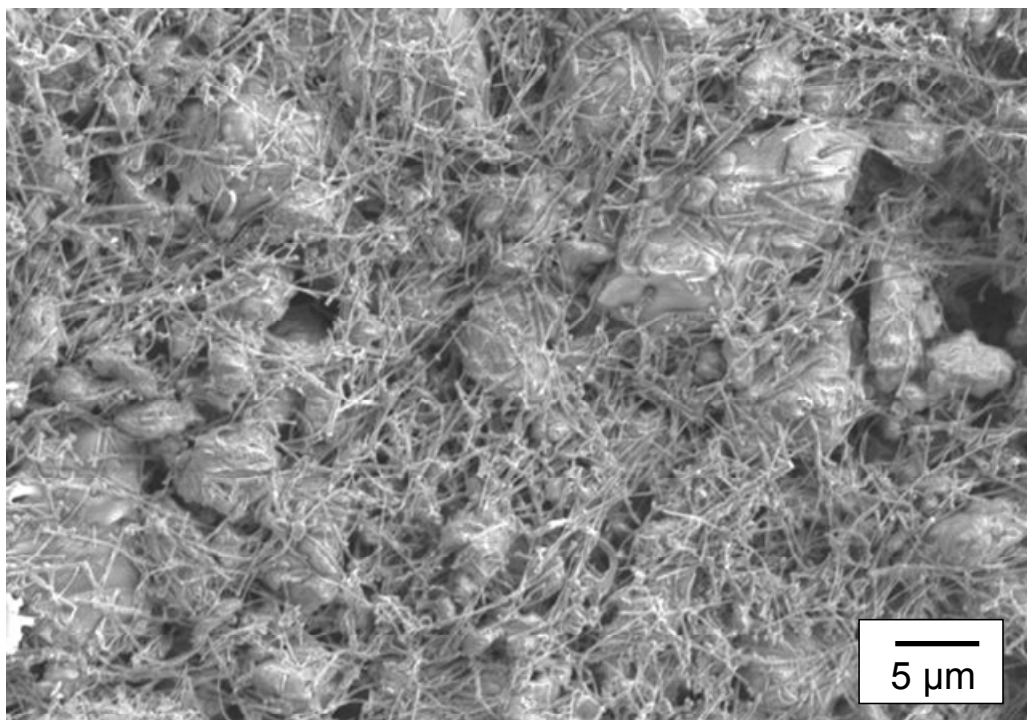


Figure 1. SEM image of the PTVE/VGCF composite electrode containing 80 wt% PTVE and 15 wt% VGCF.

Electrochemical Properties of the Polymer Electrode

A CV of the fabricated PTVE/VGCF composite electrode (80 wt% PTVE) is shown in Figure 2.

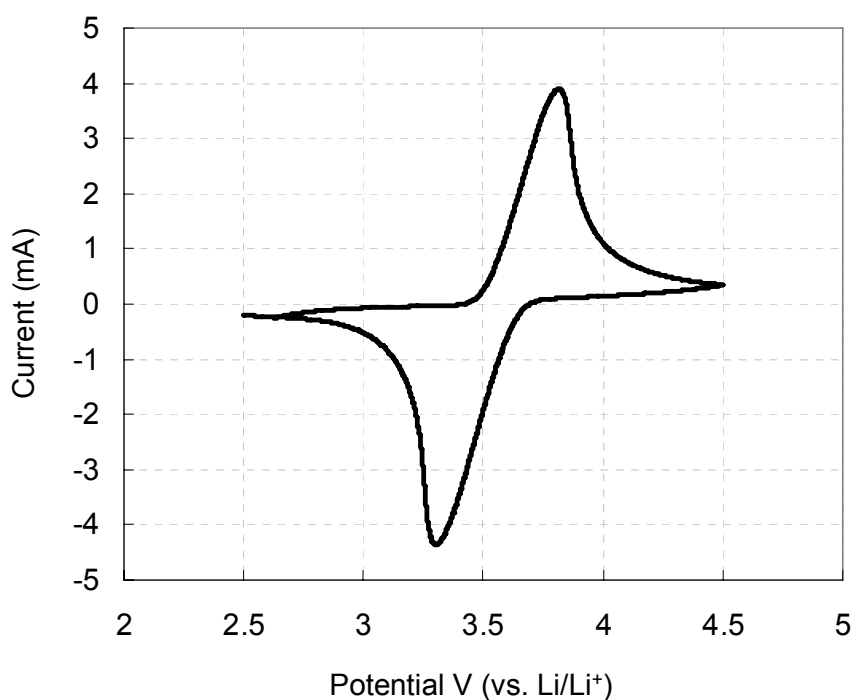


Figure 2. Cyclic voltammogram of a PTVE/VGCF composite electrode with 80 wt% PTVE and 15 wt% VGCF. The scan rate was $1 \text{ mV}\cdot\text{s}^{-1}$. Conditions: $1 \text{ mol}\cdot\text{L}^{-1}$ LiPF_6 in propylene carbonate was used as the electrolyte, Li was used as the counter electrode, and Li/Li^+ reference electrodes were used.

The oxidation and reduction potentials of the PTVE were respectively 3.81 and 3.30 V, making the estimated redox potential (vs. Li/Li^+) 3.55 V. This is consistent with a redox potential previously reported for PTVE 20 wt% electrode⁴ and is also close to the redox potentials reported for TEMPO¹⁰ and PTMA.³ However, the peak separation of this electrode is wider than that of the PTVE 20 wt% electrode. This wider peak separation of the PTVE 80 wt% electrode compared with the PTVE 20 wt% electrode can be explained by the lower amount of electron conductive material in the electrode. The

area under the oxidation peak is almost equal to that under the reduction peak, indicating excellent redox efficiency.

Charge/Discharge Properties of the Coin-shaped Cell

The first charge and discharge curves for the coin-shaped cell using the composite cathode containing 80 wt% PTVE are shown in Figure 3. The current density was set to $0.3 \text{ mA}\cdot\text{cm}^{-2}$, which corresponds to the 1 C rate of the cell. An obvious flat plateau is seen for both the charge and discharge processes. The average discharge voltage was 3.50 V. The first discharge capacity of a half-cell with a PTVE/VGCF composite electrode containing 80 wt% PTVE was $104 \text{ mAh}\cdot\text{g}^{-1}$. Since the theoretical capacity of PTVE is $135 \text{ mAh}\cdot\text{g}^{-1}$, this value means that 77% of the radicals contributed to a one-electron reaction. We previously reported that the discharge capacity of a half-cell with a PTVE/VGCF composite electrode containing 20 wt% PTVE was $114 \text{ mAh}\cdot\text{g}^{-1}$.⁴ Although the charge-discharge efficiency of the 80 wt% PTVE electrode is slightly lower than that of 20 wt%, the actual capacity of the 80 wt% PTVE electrode would be four times as large as that of 20 wt% electrode. It is surprising that the charge/discharge efficiency of 80 wt% electrode was almost the same compared with 20 wt% electrode. These results indicate that the 80 wt% PTVE electrode has a clear advantage compared with the 20 wt% one. The actual capacity of 80 wt% PTVE electrode is the highest ever reported for a cell with an all-organic-radical cathode.

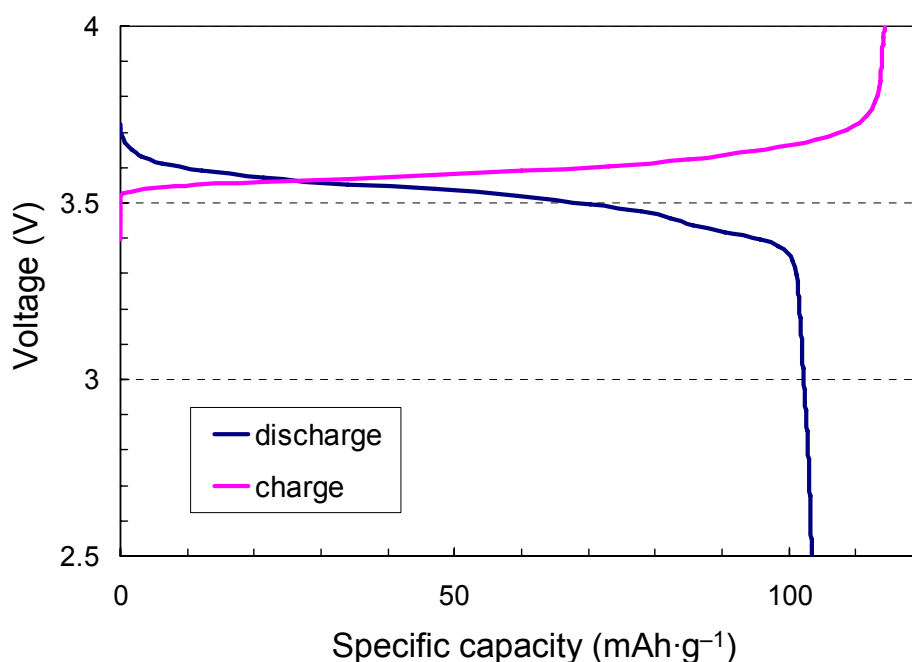


Figure 3. Initial charge/discharge curves, at 25 °C, of a Li/PTVE half cell with a cathode containing 80 wt% PTVE. The charging/discharging was carried out at a constant current density of $0.3 \text{ mA}\cdot\text{cm}^{-2}$ (1 C) in the voltage range of 2.5–4.0 V.

We also measured the rate dependences of the half-cell with an electrode containing 80 wt% PTVE. Discharge curves in the voltage range from 0.3 $\text{mA}\cdot\text{cm}^{-2}$ (1 C) to 24 $\text{mA}\cdot\text{cm}^{-2}$ (80 C) measured at 25 °C are shown in Figure 4. All charging processes were performed at the $0.3 \text{ mA}\cdot\text{cm}^{-2}$ (1 C) rate. Higher discharge rates caused a decrease in the voltage during discharge and a degradation of the capacity. When the cell was discharged at $9.0 \text{ mA}\cdot\text{cm}^{-2}$ (30 C), its capacity was 52% of the capacity at 1 C. It is surprising that 32% of the $0.3 \text{ mA}\cdot\text{cm}^{-2}$ (1 C) capacity was obtained even at the current density of 24 $\text{mA}\cdot\text{cm}^{-2}$ (80 C). The observed rate dependence shows that the

polymer-rich electrode could discharge over 50% of the cell capacity in two minutes and over 30% within one minute. These excellent high-rate properties would be attributed to the smoothness of electron transfer between PTVE and VGCF. It is surprising that the VGCF/PTVE composite electrode, which contains over 80 wt% of insulating polymer, can discharge at extremely high current density.

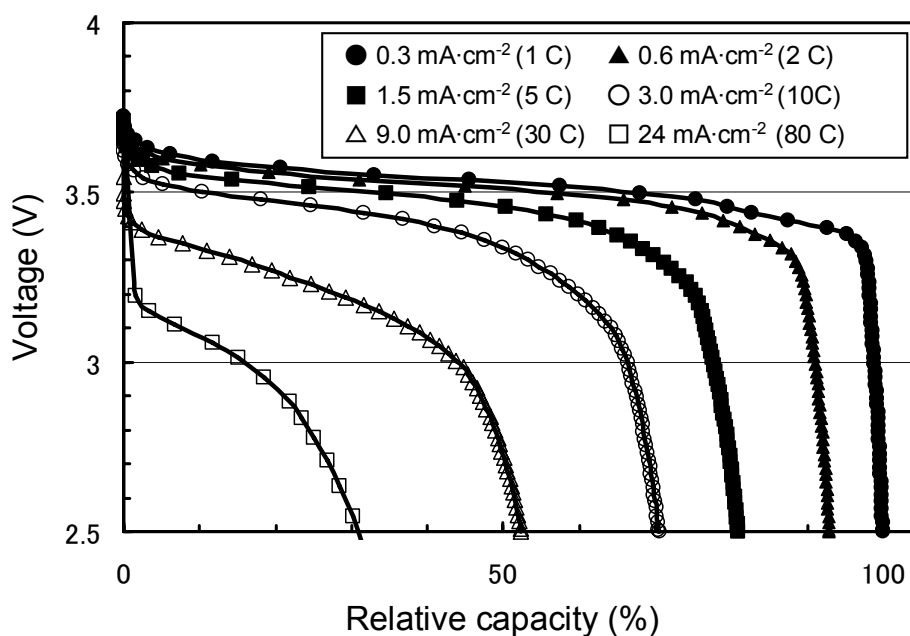


Figure 4. Discharge rate capabilities, at 25 °C, of a Li/PTVE half cell with a cathode containing 80 wt% PTVE. The charging was carried out at $0.3 \text{ mA}\cdot\text{cm}^{-2}$ (1 C).

5.4 Conclusion

A practical and polymer-rich electrode was fabricated by means of a water-based slurry method. The measured capacity of a cell made with this electrode is the highest ever reported for a cell with an all-organic-radical cathode. The work reported here is part of our efforts to develop organic radical batteries with both high capacity and high charge/discharge rates. The high capacity and excellent high-rate properties of PTVE indicate that it will have a wide range of potential applications in new power sources.

5.5 References

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Chapter 6

Summary and Prospects

Summary and Prospects

Through the present Thesis, the Author has exploited new transition-metal-catalyzed reactions, redox-active polymers, and electrodes for rechargeable batteries.

Silicone has been widely used as an industrial material with unique characteristics due to its thermal and chemical stability. In **Chapter 1**, the Author found that silicone compounds, which are commercially available and sufficiently stable in ambient atmosphere, can be used as coupling reagents for carbon-carbon bond-forming reactions. The Author also revealed that silicone compounds bearing an aryl or alkenyl group is a practical organosilicon reagent for palladium-catalyzed cross-coupling reactions. Silicone compounds are suitable as reagents for organic reactions because of their low cost, low toxicity, and easy availability. Although the reactivity of organosilicon compounds as coupling reagents is lower than that of organoboron and organotin compounds, they have recently been improved. The Author believes that silicone could be a versatile reagent for carbon-carbon bond-forming reactions in the near future.

Lithium-ion rechargeable batteries are used in portable electronic devices such as cellular phones and laptop computers. However, LiCoO_2 , which is used as a cathode-active material, in these batteries presents problems in terms of cost, toxicity, and thermal safety. The Author also described that silicone was used as a cathode active material for rechargeable battery in **Chapter 2**.

Although a number of silicone compounds with various organic substituents are readily available, they have not been studied and used as battery material. The Author

succeeded in synthesis of two kinds of TEMPO-substituted silicone compounds using a Si-H bond (PMHS) in the presence of a platinum- or rhodium-catalyst. This is the first successful transition-metal-catalyzed hydrosilylation and dehydrogenative alcoholysis of silicone with radical compounds. Furthermore, the electrochemical measurements using silicone-based TEMPO polymers as cathode active material were performed. As a result, the reversible redox and a charge/discharge plateau of TEMPO-substituted silicone were observed. This is also the first use of silicone-based polymers as an electrode active material.

In **Chapter 3**, the synthesis of a vinyl ether monomer bearing a TEMPO radical moiety and the corresponding polymer (PTVE) were described to increase the battery capacity. The TEMPO-substituted vinyl monomer was synthesized by iridium-catalyzed transvinilation of TEMPO-OH with vinyl acetate. The Author revealed that the iridium-catalyzed transvinilation was not interfered by TEMPO radical moiety. Furthermore, the Author found that cationic polymerization of a TEMPO-substituted monomer proceeded in a good yield. Since cationic polymerization of radical monomers has not yet been reported, this is the first example of cationic polymerization using TEMPO-substituted compounds. Reversible redox and a charge/discharge plateau of PTVE were observed with electrochemical measurements. The observed capacity of PTVE was much higher than that of methacrylate- and silicone-based polymers.

The studies of high-rate and high-power discharge properties were also revealed in **Chapter 4**. A copolymerized PTVE was synthesized using a vinyl monomer bearing a TEMPO radical moiety and one bearing a tri(ethylene oxide), which is known as a

higher lithium-ion conductive substituent. The high-rate and high-power discharge properties of PTVE were improved by the substitution of tri(ethylene oxide) in the PTVE's side chain. The extremely high-rate and high-power properties of the copolymerized PTVE compared with the homopolymer can be explained by the higher ion conductivity of the copolymerized PTVE.

Furthermore, for mass-produce devices at a low cost, it is necessary to develop the fabrication processes. Even if the devices are sufficiently useful, a device cannot be ubiquitous as long as the fabrication cost is high. For a new device to be widely available, it is particularly important to develop new fabrication processes. The Author believes that it is extremely important to unite reaction technologies, functions, devices, and processes to develop new devices. In **Chapter 5**, the Author described his studies on the fabrication process of high-capacity polymer/carbon hybrid electrodes. Since battery capacity significantly depends on the amount of active material in the electrode, the Author fabricated a far more polymer-rich polymer/carbon composite electrode. The Author described the fabrication process of a practical and polymer-rich PTVE/VGCF composite electrode containing 80 wt% PTVE. The results of CV measurements and the high-rate charge/discharge characteristics of the Li/PTVE coin-shaped battery were also described. The fabricated polymer-rich electrode has a larger capacity than any other organic radical electrode.

Organic materials, rather than transition metal oxides, as cathode active material of rechargeable batteries make their fabrication process and use more environmentally friendly. Humans have recently been faced with environmental and energy shortage

problems. Energy issues are not only economic problems but also environmental problems. The Author would like to contribute to solving these problems through this study.

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Chapter 1

1. Silicone as a New Class of Organosilicon Reagent for the Palladium-Catalyzed Cross-Coupling reaction

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Chapter 4

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2. Synthesis and Battery Properties of Poly(vinyl ether) Bearing a TEMPO Radical: A New Cathode Active Material for Organic Radical Batteries

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