Synthesis of Electron-Acceptor Type Redox Polymers for High-Density Charge-Storage Nanocomposites

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Wonsung CHOI
Promoter:  Prof. Dr. Hiroyuki Nishide
Referees:  Prof. Dr. Tetsuya Osaka
          Assoc. Prof. Dr. Kenichi Oyaizu
          Prof. Dr. Kurt E. Geckeler
Negatively charged organic compounds are generally unstable. Reduced state of organic molecule formed radical anion or closed-shell anion highly reactive to ambient condition such as water, oxygen, and other organic materials. Therefore, stable electron acceptor-type organic compounds are regulated to few examples compared to electron donor-type compounds. Electrical or electrochemical applications composed of organic materials were forced to rely on the few molecules. In this thesis, the author demonstrated new electron acceptor-type organic materials based on our findings for stable redox behavior of electron acceptor-type molecules in each redox centers and investigated them toward organic based high-density charge-storage systems.

Electrochemical energy storage systems play an indispensable role for portable applications, electric vehicles, and electrical power conversion systems. An attempt to realize rechargeable batteries using organic materials is a developing approach. The concept of organic-based rechargeable batteries started from the utilization of p-type doping of $\pi$-conjugated polymer as cathode reaction and was first introduced by discovery of doped polyacetylene in the late 1970s. The redox potential of conjugated polymers was floating and highly depended on charged or discharged state, which was obvious disadvantage as a battery. Redox polymer which was defined as a group of polymers consisting of non-conjugated backbone and localized redox centers could overcome the disadvantage. An unprecedented example of poly(2,2,6,6-tetramethylpiperidine-oxy methacrylate) demonstrated high charge-density as a cathode-active material. Given that power density of batteries was product of charge-density and electromotive force, large band gap between redox potentials of electrode-active materials and high charge density is the key for high power density. Now the performance of the totally organic battery was limited by stagnation of development of anode-active materials and conductive additives.

Toward high-density charge-storage electrode, this thesis focused on synthesis of new electron acceptor-type material and diminishing the conductive carbon material. Chapter 1 reviews the recent researches on electron acceptor-type material. Chapter 2 describes electrochemical property of anthraquinone derivatives. Chapter 3 describes synthesis of polyanthraquinone for high-density charge-storage. Chapter 4 describes polyimide for new n-type applications. Chapter 5 describes single-walled nanotubes for excellent conductive material. Chapter 6 describes a new charge-storable conductive material. The last chapter lists the conclusions of this thesis and displays the future prospects of the electron-acceptor type polymers.

Wonsung Choi
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Chapter 1

General Introduction

1.1 General Introduction

Negatively charged organic compounds are generally unstable. Reduced state of organic molecule, which should be radical anion or closed-shell anion, is highly reactive to ambient condition such as water, oxygen, and other organic materials. Therefore, stable electron acceptor-type organic compounds are regulated to few examples compared to electron donor-type compounds. Electrical or electrochemical applications composed of organic materials were forced to rely on the few molecules. In this thesis, the author demonstrated new electron acceptor-type organic materials based on our findings for stable redox behavior of electron acceptor-type molecules in each redox centers and investigated them toward organic high-density charge-storage systems.

Electrochemical energy storage systems play an indispensable role in these applications. They serve for portable applications, electric vehicles, and electrical power conversion systems. Attempts to achieve rechargeable batteries by using organic materials are developing approach. The concept of organic rechargeable batteries started from the utilization of p-type doping of \( \pi \)-conjugated polymer as cathode reaction. It was promoted by discovery of doped polyacetylene in the late 1970s. However, the redox potential of conjugated polymers was indistinct and highly depended on charged or discharged state. It was clear disadvantage as a battery. Redox polymer which was defined as a group of polymer with non-conjugated backbone and localized redox centers broke down the disadvantage. Poly(2,2,6,6-tetramethylpiperidine-oxy methacrylate) demonstrated high charge-density as a cathode-active material derived from redox reaction between nitroxide radical and oxoammonium cation of the redox center. Fabrication of totally organic battery whose electrode-active materials consisted of organic materials required a new anode-active material. The performance of the totally organic battery was governed by anode-active materials; power density of batteries was determined by product of charge-density and
electromotive force, thus negative redox potential and high charge density are the key for high power density.

Toward high-density charge-storage electrode, the composition of the electrode is key factor as well as electrode-active material. The redox polymers overcoming the main drawbacks of a floating redox potential and low doping density have no electrical conductivity different from $\pi$-conjugated materials. Thus, the redox polymers ordinary shows their excellent performance as electrode-active materials when it was combined with conductive additives, but it will no doubt add to total weight and impair capacity. Carbon is old but still emerging conductive materials. It is promising material suitable for recent global requirements to sustainable development by virtue of its environmental compatibility, independence of rare earth resources, and economical advantage. Nanostructured carbon materials came into the research fields. Carbon nanotube has given us great impacts from the appearance in 1993 by Iijima et al. The unique nano-scale tube structure inspired us to investigate enormous passion, showing high-conductivity, mechanical strength, and specific structure-function relationship.

Through this chapter, the author attempted to review the background and clarify the point of argument existing in the topics of electron acceptor molecules and polymers, redox polymers, and carbon materials, toward high-density charge-storage materials.

1.2 Ambient Stability of n-Type Organic Materials

Organic materials are stable in the neutral (undoped) or slightly oxidized (p-type doped) state. The redox- or dope-reaction of organic material was shown in Scheme 1. Until now, considerable efforts have been devoted to explore stable n-type doped organic materials. However, there is no n-type material capable to store negative carriers in high density. The obstacle was stem from reduced (n-type doped) state of organic material is highly sensitive to ambient condition, which was derived from instability of organic anions, particularly of carboanions.

1.2.1 Thermodynamic Reactivity toward $O_2$ and $H_2O$

They are easily oxidized in contact with contacted material such as air. It is important to note that for most n-type material, air-sensitivity is not due to intrinsic chemical instability resulting in decomposition. Air-sensitivity for typical n-type material is due to the sensitivity of the charge carriers to trapping in ambient conditions, which seriously degrades life-time of the carriers, which govern the stability of charge-storage and transporting property. The capability to design and realize stable n-type organic material where the
charge is thermodynamically air-stable would represent an important advance in charge-storage.

\[
\begin{align*}
R^+ & \xrightarrow{+e^-} R^+ \\
R & \xrightarrow{-e^-} R^- \\
\text{p-type} & \quad \text{n-type}
\end{align*}
\]

**Scheme 1.** p- and n-type redox reactions for organic material

De Leeuw et al. discussed the ambient stability of organic semiconducting material in the concept of thermodynamic stability of the carrier. They focused on electrochemical stability, separating and ignoring stability of the material against chemical reaction from the former. According to de Leeuw’s model, negative carrier is oxidized by air, although there is an overpotential between the negative carrier and oxygen.

![Figure 1](image.png)

**Figure 1.** The potential window of reduction reaction for water and oxygen. The redox potentials of typical n-type organic material.
Possible reactions and their redox potentials $E^0$ for water and oxygen, which are the main active component in air, are shown in Figure 1. All the reactions could oxidize negative carrier of n-type doped organic materials, containing reduction of oxygen, water and their concerted reaction. These reactions are strongly dependent on the pH on solution-phase electrochemical potentials.

To take an example of C$_{60}$ which was well-known semiconducting material for electrical devices such as TFT, it showed high electron transporting property but was air-sensitive. The redox potential of C$_{60}$ (-0.55 V) were relatively more negative than O$_2$ reduction + 0.62 V (pH 7). Combining these half reactions then yields:

This redox reaction will undergo due to the free energy being negative. This implies that an n-type doped material, which can be oxidized below +0.62 V versus Ag/AgCl, is not stable towards reduction of O$_2$.

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O} \quad E = +0.62 \text{ V} \\
4\text{C}_{60} + 4\text{e}^- & \rightarrow 4\text{C}_{60}^- \quad E = -0.55 \text{ V} \\
\text{O}_2 + 4\text{H}^+ + 4\text{C}_{60}^- & \rightarrow 2\text{H}_2\text{O} + 4\text{C}_{60} \quad \Delta E = +1.17 \text{ V}
\end{align*}
\]

\[
\Delta G = -nF\Delta E = -nF[+0.62 - (-0.55)] = -113 \text{ kJ/mol}
\]

A redox reaction will occur in the direction of the reduction half-reaction with higher redox potential and, similarly, in the direction of the oxidation half reaction with lower redox potential. Therefore, C$_{60}^-$ which can be oxidized at a potential lower than the potential of O$_2$ reduction is reactive under atmosphere with a pH 7.

Contrary to the sensitivity to O$_2$ reduction, C$_{60}^-$ is stable toward the reduction reaction of water to H$_2$ (-0.61 V) shown in Figure 1. Hence, the sensitivity of C$_{60}^-$ under ambient condition is basically due to the redox reaction with wet O$_2$.

Another example is tetracyanoquinodimethane (TCNQ). The potential at which TCNQ can be reduced amounts to +0.18 V. Thin film of co-evaporated tetrathiofulvalene and TCNQ have been investigated as the active component in MISFET. The measured field-effect indicated electron conductivity. Under ambient atmosphere, the conductivity slightly decreased with time. This indicates that redox potentials in the order of about +0.5 V are required for stable n-type doping. Lifetime tests showed that the devices were still operational after few months’ exposure to air. This fact was applicable to the polypyrrole and other p-type materials. Polypyrrole can be oxidized at an redox potential of about 0V. Undoped polypyrrole is unstable under ambient conditions, and is readily oxidized. On the other hand, the redox potential of polythiophene was much higher 0.7 V. Therefore, neutral state of polythiophene is kept under ambient conditions. On the left side of Figure 1, the requirements on the redox potential in order to arrive at stable n-type doped and stable undoped p-type materials are suggested. The requirements are determined for a pH 7.
Stability of n-type doped material requires a redox potential higher than about 0 to +0.5 V. This requirement on the redox potential is that the stability of n-type doped material is dominated by the redox reaction with wet O₂. On the other hand stability of p-type material requires a more negative redox potential than 0 to +0.5 V. It is worth to note that the same is true for inorganic microelectronic devices. However, there the redox reactions involved often are kinetically prohibited, and the devices are either passivated or encapsulated to minimize exposure to wet air.

Moreover, as mentioned above the redox potentials of oxygen and water are strongly dependent on pH. The redox potential of 4-electron reduction of O₂ varies +0.20 to +0.97 V between pH 1 and 14.

1.2.2 Sensitivity toward Proton

As it was discussed in 1.2, instability of n-type organic material is stem from negative charge could be trapped by ambient conditions. Value of pKₐ could indicate sensitivity of carboanion toward proton, H⁺. An acid dissociation constant Kₐ is equilibrium constant for proton and conjugated base carboanion R⁻. Organic material generally shows the larger pKₐ, carboanion become the more sensitive to proton. Therefore smaller value of pKₐ is required for stable n-type organic material. The pKₐs of organic materials were determined directly or using strong base as follows.

\[
\text{R-H} \xrightarrow{K_a} \text{R}^- + \text{H}^+ \\
\text{R-H} + \text{B}^- \xrightarrow{K_a} \text{R}^- + \text{HB} \quad \text{pK}_a = \text{pK}_B + \log \left( [\text{RH}]/[\text{R}^-] \right)
\]

The pKₐ of ethane, cyclopropane, ethylene, cyclopropene and acetylene was shown in scheme 2. Ethane shows large pKₐ of 49, indicating instability on ambient condition. In fact, the lifetime of ethane carboanion is detectable only with in the few nano-second in organic solvent. The lower pKₐ of cyclopropane indicated that delocalization of carboanion on the three carbons hamper the reactivity to the outer proton. The s-character of the center carbon also allowed smaller pKₐ. The sp hybridized acetylide anion represent the smallest pKₐ among the C₂ compounds such as propane and propene of sp³- and sp²- hybridized carboanion.

π-Conjugation and aromaticity affects strongly to the stability of carboanions. Cyclopentadienyl anion has conjugated 6π-electron in one plane, meeting the 4n+2 electrons rule. pKₐ of phenylcyclopentadienyl anion and diphenycyclopentadienyl anion was increased. The fact indicated that the cyclopentadienyl anion was localized attributed to the aromaticity of phenyl rings.

In the multiply fused ring system, the representative structure should be expressed by the structure containing the most number of localized benzene structures. At that time, the
benzene structure could not be drawn side by side. Localized benzene structure could be expressed using dotted ring as follows. The localized benzene structures could not set side by side. Cyclopentadienyl anion adjacent to the localized benzene structure could be regulated to break the aromaticity of cyclopentadienyl anion. The large pK_a of the benzene-substituted cyclopentadienyl anion supported the assumption.

These three dinaptyl cyclopentadienyl anion showed smaller pK_a s’. The smaller pK_a meant that introduced phenyl ring allowed to draw three aromatic ring across a phenyl ring. Aromaticity conjugated with carboanion stabilized the sensitivity of carboanion to proton.

\[
\begin{align*}
\text{pK}_a & \quad 15 & 18.5 & 22.9 & 23 \\
\end{align*}
\]

\[
\begin{align*}
\text{pK}_a & \quad 16.8 & 17.5 & 21.4 \\
\end{align*}
\]

1.3 n-Type Charge-Transporting and -Storage Materials

Much attention has been devoted to develop the ambient stable n-type organic materials. The design, synthesis, and performance of n-type organic material involve many different scientific issues and the related literature is disseminated over a wide variety of fields such as organic electroluminescent, thin-film-transistor, and energy-storage devices. Here, the it would be necessary to try to consolidate this literature in order to evaluate the various strategies required to the ambient stable n-type organic materials.

1.3.1 n-Type Small Molecules

The n-type organic materials are of interest to researcher of organic semiconductor. The capability to design and realize n-type semiconductors where the charge carriers are air-stable would represent an important advance in n-type electronics. Specifically,
semiconductors could be tailored to have improved solubility and film-forming properties without concern for risking atmospheric exposure. The development of air-stable materials is crucial to avoid costly vacuum/inert atmosphere-based fabrication steps and device encapsulation. One of the major challenges confronting the field of organic electronics has been the development of high-mobility and environmentally stable electron-transporting (n-type) organic semiconductors for thin film device structures to complement the high efficiency/robust nature of current generation p-type materials. One of the major hurdles remaining is the sensitivity of n-type charge carriers to ambient conditions.

Therefore, considerable efforts have been devoted to develop electron-transporting material. As was discussed, air-instability is not due to intrinsic chemical instability resulting in material decomposition, but rather, air-instability for typical n-type semiconductor is due to the sensitivity of the charge carriers to trapping in ambient conditions, which seriously degrades effective field-effect mobility, and which is frequently reversed upon application of vacuum. Rational strategies for increasing ambient stability must design molecules/polymers to resist to trapping thermodynamically. Otherwise, charge-transporting area of the film should be kept from trapping species. Thermodynamic stability is thought necessary to stabilize the charge carriers in n-type organic materials with respect to reduction of O₂ at +0.62 V. It is generally thought that H₂O/O₂ exclusion can be facilitated by utilizing molecular semiconductors which crystallographically pack in a sufficiently dense motif so as to resist film penetration by these species or by appropriately encapsulating the devices in inert atmosphere.

![Chart 1](image)

The most investigated air-stable n-type organic semiconductors include perfluorinated copper phthalocyanine (CuF₁₆Pc),⁴ fluoroacyl oligothiophenes (DFCO-4TCO),⁵ N,N'-fluorocarbon-substituted naphthalene diimides (NDI-F, NDI-XF),⁶ cyano-substituted perylene diimides (PDI-CN₂, PDI-FCN₂),⁷ and cyano-substituted naphthalene diimides (NDI-8CN₂). With the exception of imide-substituted oligo-naphthalenes, the NDI and PDI derivatives, the electrical performance of TFT devices fabricated with these air-stable
materials does not approach that of high mobility but of air-sensitive materials such as C$_{60}$, PDI-8, PDI-13, FT(Th)$_2$TF, DFHCO-4T, DFCO-4T, and DCMT.

For the robust, tunable LUMO character and high semiconductor performance, members of the arylene imide family are particularly attractive target materials to explore. The ambient stability in these semiconductors could be achieved by two different strategies: (i) introduction of fluorinated substituents ($R^F$) at the $N,N'$ positions to create close-packed solid state atmospheric barriers or (ii) addition of highly electron-withdrawing substituents, thereby lowering the energies of the LUMO/charge carriers below that of most atmospheric trapping species.

![Chart 2: Air-unstable n-type organic semiconductors.](image)

In the case of NDI-F or asymmetric derivatives with single $R^F$ chain, Katz et al. proposed that the concept of “O$_2$ barrier”. The addition of fluorocarbon substituents to the $N,N'$ positions does not significantly lower the molecular reduction potentials relative to the fluorine-free analogues; relative to the fluorine-free analogues; however, OFETs fabricated with films of the fluorinated materials are reported to exhibit air-stable device operation while the fluorine-free analogues do not. Since the $R^F$ chains do not significantly alter the LUMO energies of these NDI derivatives ($\Delta E \leq 0.15$ eV), asteric barrier to atmospheric penetration created by the densely packed RF groups is thought to be responsible for the charge carrier air stability. Furthermore, in the case NDI-XF, the reduction potential is also nearly identical to that of the non-fluorinated derivative. In this case as well, only the fluorinated materials exhibit ambient OFET stability. Recently, PDI-based materials with fluoro-substituted phenyl groups at the $N,N'$ positions were shown to yield air-stable OFET operation despite having similar reduction potentials to the non-fluorinated parent. Interestingly, the air stability was also shown to be dependent on the fluorination level and fluorine substitution pattern. Katz et al. explained that the lager fluorine van der Waals...
radius relative to hydrogen leads to a decreased available spacing between the \(N,N'\)-chains from \(\sim 4\ \text{Å}\) to \(\sim 2\ \text{Å}\), thus preventing \(O_2\) intrusion.

In the case of \(\text{CuF}_{16}\text{Pc}\), the air-stable device behavior is thought to reflect a combination of a close-packing \(O_2\) barrier and the low-lying LUMO of the material. The analogous chlorinated material, \(\text{CuF}_{16}\text{Pc}\), is also reported to support air-stable OFET operation because of the low-energy charge carriers. Non-fluorinated air-stable organometallic- and fullerene-based semiconductors with LUMO energies more negative than \(\sim -4.0\ \text{eV}\) also show resistance to air-derived electron traps.

![Figure 2](image)

**Figure 2** Space-filling model of PDI-based dimers taken from the published crystal structure. The model of air-unstable \(N,N'\)-n-pentyl-PDI (a) depicts the channels between hydrogen atoms of adjacent hydrocarbon \(N,N'\)-groups. The model of air-stable PDI-FCN\(_2\) (b) depicts the substantial contraction of the channels between the fluoroalkyl chains.

Recently, T.J. Marks et al. reported ambient operational stability and high carrier mobility in the cyanated perylene diimides, \(\text{PDI-CN}_2\) and \(\text{PDI-FCN}_2\), and cyanated naphthalene diimide \(\text{NDI-8CN}_2\). While \(\text{PDI-FCN}_2\) has fluorinated functionalities that can provide a barrier analogous to the aforementioned air-stable materials, the \(N\)-hydroalkyl functionalized structures of \(\text{PDI-CN}_2\) and \(\text{PDI-FCN}_2\) are unique among air-stable n-type organic semiconductors because the \(N\)-alkyl groups (\(R^H\)) cannot provide the same kind of barrier to atmospheric electron traps as the \(N\)-\(R^F\) chains.

In addition to these results, has documented the air instability of \(N\)-alkyl PDI and NDI derivatives. Thus, Malenfant et al. demonstrated that OFETs fabricated with \(N,N'\)-n-octyl PDI derivatives possess excellent electrical properties but that the performance degrades rapidly in air. Furthermore, the same behavior is observed in \(N,N'\)-n-octyl NDI derivatives. More recently, Bao et al. reported that \(N,N'\)-cyclohexyl PDI devices also fail in air. Frisbie et al. shed light on the mechanism of such device failures by increasing the \(O_2\) partial pressure in the operating atmosphere for OTFT devices fabricated with \(N,N'\)-n-pentyl PDI derivatives and reported a positive shift in threshold voltage with increasing \(O_2\) partial pressure during operation. This can be assigned to the creation of metastable PDI/O\(_2\) trap
states. Given that O$_2$-derived trap formation in arylene diimide semiconductor films is found to occur when the $N,N'$ substituents are either saturated, it would appear that the mechanism for air stability in the analogous cyano-substituted materials (PDI-CN$_2$ and NDI-8CN$_2$) is markedly different from that invoked in the case of the aforementioned $N$-fluorocarbon materials.

These n-type organic materials all consisted of small molecules. One of the important advantages of the organic materials come from facile processability by virtue of solubility and film-forming properties. However, these molecules require high crystalinity and packing properties. Therefore, development of electron acceptor-type polymers having electron-transporting, -charging property is attractive challenge for organic electrical and electrical energy storage devices.

1.3.2 n-Type $\pi$-Conjugated Polymers

The concept of n-type organic material is introduced to $\pi$-conjugated polymer in early 1990s, through the development of organic electroluminescent devices. MEH-2CN-PPV was synthesized by Knoevenagel reaction, introducing typical electron-withdrawing cyano group into MEH-PPV backbone. MEH-2CN-PPV showed a very high photoluminescence efficiency of 60% as well as 4% external efficiencies. The improved device property has been attributed to the cyano groups that facilitate electron injection. MEH-2CN-PPV could show photo-emitting property combined with phenylenevinylene units at a composition of less than 10% of loading ratio. The conjugated polymers were tailored to be soluble employing long and/or branched alkyl chains.

![Scheme 1. Synthetic route of MEH-2CN-PPV by arranged Wittig reaction.](image)

The cyano-substituted vinylene units are intrinsically unstable and can be easily photooxidized, while the introduction of cyano group on the phenylene ring of the PPVs results in more stable polymers. Another approach to synthesize cyano-substituted PPV was reported as DOCN-PPV for organic solar cells in 2000s, where cyano groups were
substituted to the phenylene units on behalf of vinylene unit.\textsuperscript{15} In addition to the high stability against the photoxidation, the DOCN-PPV exhibited long wavelength adsorption attributed to charge-transfer at \( \lambda_{\text{max}} > 450 \) nm and crystallinity due to regioregularity of alkyl side chains, which was expected to be applicable for organic bulk heterojunction photovoltaic cells.

\[ \text{NCOC}_{8}H_{17} \]
\[ \text{C}_{8}H_{17}OC \]
\[ \text{NCOC}_{8}H_{17} \]
\[ \text{Br} \]
\[ \text{Br} \]
\[ \text{NC} \]
\[ \text{CN} \]
\[ + \ (C_{4}H_{9})_{3}\text{Sn=Sn(C}_{4}H_{9})_{3} \]
\[ \rightarrow \]
\[ \text{OC}_{8}H_{17} \]
\[ \text{C}_{8}H_{17}OC \]
\[ \text{NC} \]
\[ \text{OC}_{8}H_{17} \]
\[ \text{Br} \]
\[ \text{Br} \]
\[ \text{NC} \]
\[ \text{CN} \]
\[ \text{DOCN-PPV} \]
\[ -1.06 \text{V} \]

**Scheme 2.** Synthetic route of DOCN-PPV by Stille coupling

**Chart 3** (a) Structure and reduction potential of the heterocyclic compounds, (b) representative example of the polymer containing heterocyclic moiety.

In 1990s, a series of electron-acceptor type polymers containing heterocyclic moiety in the back bone was synthesized by cross-coupling reactions. The heterocyclic compounds, i. e. pyridine, quinoline, anthrazoline, and phenadine, showed relatively negative redox potentials (<-1 V) in organic materials approaching to the potential window of general organic electrolyte such as acetonitrile.\textsuperscript{16} Even though they have exhibited strong electron
affinity, they were air-unstable and could not show reoxidation peak after electrochemical reduction, indicating decomposition of the material in the electrolyte rather than solubilization. Moreover, electrochemically reduced compounds are highly reactive to O$_2$ due to the negative potential (<-0.5 V). These results made it difficult to utilize heterocyclic compounds as a redox center.

The first report of an n-channel FET-active polymer was Poly(benzobisimidazobenzophenanthroline) (BBL), a ladder-type polymer. BBL can be prepared by a polar methanol solution containing methanesulfonic acid to form nanobelt-structure. The synthesis of BBL has been reported by R. L. Van Deusen in 1969. At that time, however, BBL was just prepared in the solid state. Jenekhe et al. found that BBL hardly soluble in general solvent was solubilized by a strong acid, methanesulfonic acid, as a solvent in 1990. The solubilized BBL self-assembled rapidly after adding CHCl$_3$/CH$_3$OH mixture to form nanobelt. The ladder structure of the BBL allowed 1D nanostructure. Face-to-face packing of the large $\pi$-conjugated plane perpendicular to the nanobelt axis was indicated by X-ray diffraction analysis and TEM. The 1D structure allowed unprecedented air-stability and high electron mobility for over 200 days even though the LUMO appeared at 4.0 eV, which could respond to -0.5 V (vs. Ag/AgCl) much negative than O$_2$ reduction (<0.6 V). The excellent air-stability might be derived from the close packing to prevent O$_2$ intrusion. The concept of O$_2$ blocking is adapted for n-type polymer. However, the low solubility and requirement of acid treatment still hampered the practical use of BBL.

![Chemical structure of BBL and crystal structure of BBL nanobelt.](image)

The preparation strategy of “O$_2$ barrier” has attracted a considerable amount of OFET researchers. The bithiophene back bone exhibited a high packing property and high electron conductivity, which was typically employed as a building block. Polybithiophenes containing various imide groups such as PIDT were synthesized. But very few numbers of the polymers succeeded in realizing soluble n-type semiconductor behavior. PBI showed a n-type charge mobility but degraded quickly under ambient air exposure. P-IFDMT4 bearing ladder structure indenofluorenebis(dicyanovinylene) moiety was reported by Facchetti and Tobin J. Marks. Solution-processed FET was prepared and exhibited high electron mobility and air-stability.
To overcome the early attempt to prepare n-type polymer based on N-heterocyclic electron-deficient aromatics, which has met a limited success. Poly(pyridinium Phenylene)s were reported by Swager et al.\textsuperscript{24,25} Instead of the neutral nitrogen containing heterocyclic moiety, the polymer contained electron-deficient pyridinium rings. Swager et al. insisted that reduction (n-type doping) of the polymer exhibited high conductivity (9 S/cm) though the neutral polymer showed no conductivity. In addition, the polymer quenched PL spectra of MEH-PPV in a bilayer device of the polymer and MEH-PPV.

\[
\text{Poly(pyridinium phenylene)} \\
E_{\text{red}} = -0.51 \text{ V}
\]

The n-type $\pi$-conjugated polymers with a 1,2,4-triazole ring substituted by a benzo-15-crown-5ether subunit at the 4-position of the 1,2,4-triazole ring (TP-T-benzo15C5)\textsuperscript{26} were synthesized by organometallic polycondensation. The polymer with the benzo 15C5 subunit exhibited a considerably higher stability of the n-doping state in air than that without this subunit. Conductivity of the n-type doped polymer were maintained when sodium cation was employed as counter cation.

\[
\text{TP-T-benzo15C5} \\
E_{\text{red}} = -2.37 \text{ V}
\]

Various viologens have been used to control the doping of single-walled carbon nanotubes (SWCNTs) via direct redox reactions.\textsuperscript{27} A new method of extracting neutral viologen was introduced using a biphase of toluene and viologen-dissolved water. A reductant of sodium borohydride transferred positively charged viologen ($V_2$) into $V_0$. 

where the reduced $V^0$ was separated into toluene with high separation yield. This viologen change all the p-type CNT into n-type. The yielded n-type CNTs were stable in water, which act as a protecting layer to prevent further oxidation from water.

1.3.3 n-Type Redox Polymers (Non $\pi$-Conjugated Polymer)

There were several attempts to apply redox polymer for charge-storage material, where redox polymer meant the polymer bearing redox centers as pendant group in aliphatic backbone hereinafter. The redox centers governed the electrochemical property of the polymer such as redox potential. The mechanism of propagation was different from field-effect induced electron transfer.\(^3\) Charges propagated by electron-exchange reactions between redox-centers accompanied by counterion transfer. Ion accommodation was facilitated by the amorphous aliphatic backbone, which allowed high degree of doping. The deep doping could lead to the high charge-discharge capacity as a charge-storage device.

![Figure 4](image)

**Figure 4.** The illustrative map of the redox potentials versus the formula weight-based capacities of p- and n-type radical polymers. Work functions were translated from the absolute potentials $E_{\text{abs}} = E^\circ$ + 4.66 V versus vacuum, where $E^\circ$ was approximated by formal potentials obtained from cyclic voltammetry versus Ag/AgCl.
Nishide et al.\textsuperscript{28} first reported the organic charge-storage device prepared by employing p- and n-type redox-active polymers as a cathode- and anode-active material, respectively. A series of radical was selected for redox center which was in nature highly reactive but so-called robust radical was employed for the centers. Robust radical was able to stable under ambient condition because usually the unpaired electron was sterically hindered. A number of radical polymers were synthesized and applied to the charge-storage device. The redox potential and capacity was shown in Figure 4. The radical polymers showed excellent charge-storage performance represented by poly(2,2',6,6'-tetramethylpiperidinoxy-methacrylate) (PTMA) as a cathode-active material based on the rapid electron transfer reaction. After unprecedented finding of the PTMA, much attention was paid to synthesize n-type radical polymer complementary as an anode-active material. Substitution of electron-withdrawing group such as fluorinated alkyl group to nitroxide radical allowed n-type redox properties of the radical moiety. Nitoronyl nitroxide radical showed both p- and n-type redox ability.\textsuperscript{29,30} The operations of radical polymers bearing n-type redox active radicals as anode-active materials were reported. However, the low capacity of these n-type redox active polymers limited the total capacity of the organic charge-storage device. Moreover, the cyclability of the charge-storage device was suppressed by the elution of the reduced n-type radical polymer. In general, reduced polyanion was highly soluble. Therefore, the development of n-type redox-active polymer was attractive issue now.

1.4 Organic Electron-Transfer Reaction

The redox center governs the redox potential and the heterogeneous rate constant. Therefore, design of the center could be a key of redox-polymer design. Reversible redox, rapid electron transfer and small formula-weight of redox center are required for stable n-type redox polymer. In this section, the author would like to summarize electron transfer reaction of small molecules which could be a redox center.

1.4.1 The Marcus Microscopic Model\textsuperscript{32}

In redox polymer, redox centers in the pendant groups undergo homogeneous reduction of O to R (Figure 5).

\[ O + R \rightarrow R + O \]

It is easy to consider the two situations in the same theoretical context. Electron-transfer reactions, whether homogeneous or heterogeneous, are radiationless electronic rearrangements of reacting species. Since the transfer is radiationless, the electron must move from an initial state (O or R in the left) to a receiving state (R or O in the right) of the same energy. This demand for isoenergetic electron transfer is a fundamental aspect with
extensive consequences.

Figure 5. Self-exchange electron transfer in redox polymer

Electron transfer is the assumption that the reactants and product do not change their configurations during the actual act of transfer. This idea is based essentially on the Frank-Condon principle, which says, in part, that nuclear momenta and positions do not change on the time scale of electronic transitions. Thus, the reactant and product, O and R, share a common nuclear configuration at the moment of transfer.

Figure 6. Standard free energy, $G^0$, as a function of reaction coordinate, $q$, for an electron transfer reaction, such as $O + e^- \rightarrow R$. This diagram applies either to a heterogeneous reaction in which O and R react at an electrode of a homogeneous reaction in which O and R react with members of another redox couple.

We consider the reaction as occurring on a multidimensional surface defining the standard free energy of the system in terms of the nuclear coordinates (i.e., the relative positions of the atoms) of the reactant, product, and solvent. Changes in nuclear coordinates come about from vibrational and rotational motion in O and R, and from fluctuations in the position and orientation of the solvent molecules. As usual, we focus on the energetically favored path between reactants and products, and we measure progress in terms of a reaction coordinate, $q$. Two general assumption are (a) that the reactant, O, is centered at some fixed position with respect to the electrode (or in a bimolecular homogeneous reaction, that the reactants are at a fixed distance from each other) and (b) that the standard free
energies of O and R, $G^0_{O}$ and $G^0_{R}$, depend quadratically on the reaction coordinate, $q$.

\[
G^0_{O}(q) = (k/2)(q - q_O)^2 \\
G^0_{R}(q) = (k/2)(q - q_R)^2 + \Delta G^0
\]

where $q_O$ and $q_R$ are the values of the coordinate for the equilibrium atomic configuration in O and R, and $k$ is a proportionality constant (e.g., a force constant for a change in bond length). Depending on the case under consideration, $\Delta G^0$ is either the free energy of reaction for a homogeneous electron transfer of $F(E-E^0)$ for an electrode reaction.

In Figure 6, for the heterogeneous case, the curve for O is actually the sum of energies for species O and for an electron on the electrode at the Fermi level corresponding to potential $E$. Then, $\Delta G^0 = F(E-E^0)$. For the homogeneous case, the curve for O is the sum of energies for O and its reactant partner, R, while the curve for R is a sum for R and O. Then, $\Delta G^0$ is the standard free energy change for the reaction. The picture at the top is a general representation of structural changes that might accompany electron transfer. The changes in spacing of the six surrounding dots could represent, for example, changes in bond lengths within the electroactive species or the restructuring of the surrounding solvent shell.

Defining $\lambda = (k/2)(q_R - q_O)^2$. The free energy of activation for reduction of O is given by,

\[
\Delta G_f^\ddagger = \frac{\lambda}{4} \left(1 + \frac{F(E-E^0)}{\lambda}\right)
\]

The critical parameter is $\lambda$, the reorganization energy, which represents the energy necessary to transform the nuclear configuration in the reactant and the solvent to those of the product state. It is usually separated into inner, $\lambda_i$, and outer, $\lambda_o$, components:

\[
\lambda = \lambda_i + \lambda_o
\]

where $\lambda_i$ represents the contribution from reorganization of species O, and $\lambda_o$ that from reorganization of the solvent. Typically, $\lambda_o$ is computed by assuming that the solvent is a dielectric continuum, and the reactant is a sphere of radius $a_O$. For an electrode reaction,

\[
\lambda_o = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{a_O} - \frac{1}{R}\right) \left(\frac{1}{\varepsilon_{OP}} - \frac{1}{\varepsilon_s}\right)
\]

where $\varepsilon_{OP}$ and $\varepsilon_s$ are the optical and static dielectric constants, respectively, and $R$ is taken as twice the distance from the center of the molecule to the electrode. (i.e., $2a_0$, which is the distance between the reactant and its image charge in the electrode). For a homogeneous electron-transfer reaction:

\[
\lambda_o = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{a_1} + \frac{1}{2a_2} + \frac{1}{a_3}\right) \left(\frac{1}{\varepsilon_{OP}} - \frac{1}{\varepsilon_s}\right)
\]
where \( a_1 \) and \( a_2 \) are the radii of the reactants (O and R’ in equation 3.6.1) and \( d = a_1 + a_2 \). Typical values of \( \lambda \) are in the range of 0.5 to 1 eV.

Assuming that the rate constant \( k_0 \) have an Arrhenius form and that \( \lambda \) is \( \lambda_o \), the rate constant can be expressed as,

\[
k_0 = Z_{ex} \exp \left( -\frac{\lambda_o}{4RT} \right)
\]

For the self-exchange reaction, \( \Delta G_0^\ddagger = 0 \), so \( \Delta G_i^\ddagger = \lambda_{ex}/4 \). For the electrode reaction \( k_0 \) corresponds to \( E = E_0 \), so \( \Delta G_i^\ddagger = \lambda_{el}/4 \), with the condition that \( \lambda_i \), is negligible. This relation is very important. It, or variation derived from it, is used in the treatment of almost every problem requiring an account of electron-transfer kinetics. One can express \( \Delta G_i^\ddagger \) for the homogeneous and heterogeneous reactions in common terms, and one find that \( k_{ex} \) is related to \( k_0 \) by the expression

\[
(k_{ex}/A_{ex})^{1/2} = k_0/A_{el}
\]

where \( A_{ex} \) and \( A_{el} \) are the pre-exponential factors for self-exchange and the electrode reaction.

1.4.2 The Redox Tunability of n-Type Organic Compounds

The early findings that stability of carboanion was tunable using aromaticity prompted it to be applied to extended \( \pi \)-conjugated system. Quinones shed insight into stable n-type redox property. Quinones undergo 2 step 2 electron reductions from neutral benzoquinone to semiquinone radical anion, and dianion in organic medium where no protonation proceeds. Quinoid structure of quinone turned to form aromatic benzenoid structure. The aromatic structure allows stable anion. Reduced quinones associated with proton to generate hydroquinone in aqueous media.

\[
\begin{align*}
Q^0 &+ e^- \rightarrow Q^- \\
Q^0 &+ e^- \rightarrow Q^{2-}
\end{align*}
\]

Localized benzene structures could prohibit formation of the localized benzene structure consisting of reduced quinones, leading to lowering redox potential. The assumption was supported by quinone derivatives containing large fused rings. Structure of quinone derivatives and their redox potentials are shown below. The redox potential of naphthoquinone and anthraquinone were lowered compared to that of benzoquinone, indicating the same effect found in aromatic carboanions. The results pave the way not only
for stabilization of anions but also for modulation of redox potential of quinones.

The general idea was introduced to various π-extended compounds containing tetracyanoquinodimethane (TCNQ). In TCNQ, electron-withdrawing dicyano-methylene group was substituted instead of oxygen atom in benzoquinone. TCNQ exhibited more negative redox potential of 0.18 V due to the strong electron-withdrawing structure than that of benzoquinone of -0.47 V. The redox potential higher than two electron reduction of O₂ at 0 V allowed air-stability compared to the instable reduced quinone as discussed.

The organic anions (n-type doped organic material) were stabilized based on both induced aromaticity and electron-withdrawing group. Following these early findings, a number of compounds are synthesized and investigated to realize bistability between doped and undoped state. Especially, stability of doped state is important for bistability.

The stabilization using aromaticity was further extended to larger π-conjugated systems, following 4n+2 rule. In addition to typical example of cyclopentadienyl anion for 6π-conjugated system, viologen showed stable n-type redox property at -0.63 V. At neutral state, nitrogen atom of viologen donates a lone pair to conjugated 6 membered ring to form 7π-conjugated system. One electron oxidation of each 7π-conjugated system generated 6π-conjugated system. The 6π-conjugated system fulfilled the 4n+2 rule for aromaticity. The two aromatic rings were linked together but shared no carbon atom, allowing maintaining aromaticity on each ring. Although viologen only consisted of two pyridinium ions, the redox potential of viologen was much higher than that of pyridinium ion, indicating delocalization of electrons on the π-conjugated system. The finding offers a clear
insight that connection of $\pi$-conjugated systems allows expanding of conjugation without losing aromaticity.

Stability of $n$-type doped state was also stabilized by $10\pi$-conjugated system of pyrindine. Pyrindine contains two nitrogen atoms, which donate two lone pairs to the conjugated system to form $8\pi$-conjugated system and $10\pi$-conjugated system at the two electron reduced state. Instability of the neutral state enables the stability of the doped state. Phenalenyl radical is a robust neutral radical. The neutral state was stabilized by structural change of open shell to closed shell. The instability of neutral radical state and the stability of the doped state allowed bistable redox property.

Nitronyl nitroxide radical showed both $p$- and $n$-type dopability at 0.80 and -0.84 V. The radical was substituted to polyacetylene, which exhibited ambipolar chargeability. Phenalenyl radical also shows a stable $p$- and $n$- dopability. Anti-aromatic phenalenyl radical was combined with phenalenyl radical to destabilize neutral state.

Expansion of effective conjugation length was one of the important factors to determine the redox potential. para-Quinones with sterically hindered keto groups have been characterized. All species exhibit two successive one-electron reductions. The quinones shown below with vinylene, phenylene, and butylene spacer exhibited -0.83, -0.61, and -0.93 V, respectively.
Chapter 1

The expanded conjugation stabilized reduced anion leading to higher redox potential. The shortest spacer allowed conjugation between two keto groups. On the other hand, quinones with butadienyl spacer, the longer spacer, showed lower potential although phenylene spacer stabilized the anion. The lower redox potential of butylene spacer indicated that distortion between keto groups could hinder the conjugation.

Although large \( \pi \)-conjugation allows multi-electron process based on stabilization of doped state, these electron transfer process has limitation that the multi-electron transfer proceed not at same potential but at several potentials. The different potential came from the Gibbs free energy of disproportionation of the intermediate. For example, the disproportionation between dianion and neutral compounds is expressed, \( A^2^- + A^- \rightarrow 2A^- \).

Destabilization of the neutral state was also introduced to successive two electron reduction to simultaneous two electron reactions. The concept was introduced as “inverted potentials in two electron process” by D. H. Evans et al.\(^{35}\) Generally, when one electron was injected to a compound such as quinone at \( E_1 \), the negatively charged state destabilize the second electron injection leading to higher redox potential \( E_2 \). According to Evans et al., if the first electron injection change the structure of compounds to stabilize the reduced state, the second reduction could be easier that the first. Dicyanomethylidene-substituted quinocyclopropene was synthesized and showed simultaneous two electron reduction at 0 V.\(^{36}\) This result provably supported the concept that one electron reduction disconnected the \( \pi \)-conjugation due to the steric hindrance to destabilize the reduced state and facilitated the second reduction. The reagent could be useful for effective two-electron oxidation reagent.

In this term, stabilization of reduced state (n-type doped state) was discussed. These investigations are all related only to the molecular structure including electron-withdrawing groups, aromaticity, \( \pi \)-conjugation, and sterical effect. Actually, these stabilization methods provided us to thermodynamically stable compounds. However, this will be no doubt that the increment of formula-weight spoiled negative potential as an anode-active material. The combination of thermodynamical instability and ambient stability was required for high density charge-storage.

Organic cationic compounds shown in Figure 7 are capable to be reduced at more positive potential than heterocyclic compounds containing nitrogen atom. The relatively positive potential allowed stable redox reaction. Acrydinium cation, an oxidized compound of
acridine, shows more positive redox potential compared to that of acridine (-1.5 V). Methylviologen (MV) has mediate negative charges as redox mediator in hydrogen producing electrode. N-methyl-6-mesitylacrydine (MeAcr)\(^\text{38}\) have maintained extremely long exited state attributed to the stable acceptor property of acridinium moiety and donor property of mesitylene as reported by Fukuzumi et al.. MeAcr showed reversible redox wave for several sweeping.

\[
\begin{align*}
\text{Acridine} & : \text{E} = -0.24 \text{ V} \\
\text{MeAcr} & : \text{E} = -0.53 \text{ V} \\
\text{Methylviologen (MV)} & : \text{E} = -0.44 \text{ V} \\
\end{align*}
\]

\[\text{Figure 7. Structures and reduction potentials of cationic organic acceptors.}\]

\[\text{1.4.3 Multi-Electron Transfer}\]

Multi-electron transfer of redox center can offer an opportunity for larger formula-weight based capacities. However, the redox polymers bearing redox center which proceeds multi-electron transfer has various hurdles. The reduction potentials gradually go negative with increasing charges, making the realization of stable n-type redox polymer featuring multi-electron transfer difficult.

The multi-electron transfer of neutral organic compounds proceeds sequentially where electrons are added successively to the reactant to form a series of ions with increasing charge. A reactant which undergoes successive two electrons reaction in two steps with its redox potential \(E_1\) and \(E_2\) are expressed

\[A + e^- \rightarrow A^- \quad E_1\]
\[A^- + e^- \rightarrow A^{2-} \quad E_2\]

The addition of electron is significantly more difficult than the first. Difference between the redox potentials could be explained by the disproportionation of \(A^-\), the combination of the two half electrode reactions.

\[2A^- \rightarrow A^{2-} + A \quad \Delta E = E_2 - E_1\]
because the Gibbs energy change for the disproportionation reaction is simply related to the difference between two

\[ \Delta_{\text{disp}}G^\circ = -nF\Delta E = RT \ln K_{\text{disp}} \]

where \( \Delta E \) is negative. Much negative potential, \( E_2 \), cause the high sensitivity to ambient condition. Therefore, \( \Delta E \) is required to approach ignorable value.

**Stabilization of Multi-Electron Transfer by Counterion.** A typical example is found with fullerenes, \( C_{60} \), which is capable of six electrons to produce the corresponding hexaanions. The reversible reductions were observed from \( C_{60} \) to \( C_{60}^{-6} \). The first and second reduction steps, \( C_{60}^{-} \) and \( C_{60}^{-2} \), are associated with two or more tetra alkyl ammonium cations. The strength of the association increased with increasing cation size. The first and second reduction reaction was expressed as below,

\[
\begin{align*}
C_{60} + e^- &\rightarrow C_{60}^- \\
C_{60}^- + n\text{TBA} &\rightleftharpoons C_{60}^-(\text{TBA})_n & K_{\text{eq}(1)} \\
C_{60}^- (\text{TBA})_n + e^- &\rightarrow C_{60}^{2-} (\text{TBA})_n \\
C_{60}^{2-} (\text{TBA})_n + (m-n)\text{ROH} &\rightleftharpoons C_{60}^{2-} (\text{TBA})_m & K_{\text{eq}(2)}
\end{align*}
\]

where the association constant \( K_{\text{eq}(2)} (>10^6) \) was much higher than \( K_{\text{eq}(1)} (>10^3) \). The fact suggested that the interaction between ammonium cation and reduced anions of \( C_{60} \) are dependent on concentration and electrostatic force.

---

**Figure 8.** Mirror image model of electrolyte effects on \( \Delta E_{1/2} = E_2 - E_1 \)
Medium Effects Tunability of $\Delta E_{1/2}(= E_2 - E_1)$ was suggested by Geiger et al.\textsuperscript{40} The effect of the solvent/electrolyte medium, has been systematically probed. Size of electrolyte cation/anion, solvent polarity, solvent donor/acceptor number, and electrolyte concentration were systematically surveyed. The $\Delta E_{1/2}$ was explained by mirror image model in Figure 8 that $\Delta E_{1/2}$ for reduction potentials was increased with large cation and large donor number, and vice versa in low polar solvent. This fact suggested that solubilization energy was inversely proportional to electric permittivity and electrostatic compensation was facilitated by smaller counterion. The role of solvents is control of ion-pairing where the most critical factor is how the solvent associate with counterion but not with the same charged ion.

Stabilization by Hydrogen-Bonding. The association reaction was observed in the case of quinones and alcohols. The association was dependent on the acidity of alcohols and basicity of quinones.\textsuperscript{31,42} Strong hydrogen bonding of alcohol with showed strong association hydrogen-bonding, which stabilized second reduction potential even though the first reduction potential showed little potential change. In contrast to the hydrogen-bonding, association between a much stronger acidic alcohol and a more basic quinone leaded to protonation of quinone showing slow electron-transfer kinetics. These association offered stabilization capability by hydrogen-bonding and clear insight to the relationship between quinones and hydrogen-donors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydrogen-bonding.png}
\caption{Hydrogen-bonding and protonation effect of electrochemistry of quinones in aprotic solvents. In square: Quinones redox behavior in various solvents.}
\end{figure}
D.K. Smith et al. shed light into the relationship between hydrogen-bonding and protonation dependent on pH. Generally, electrochemistry of quinones was investigated in buffered solution to avoid change of solution’s pH. However, buffered and unbuffered states critically affected to govern the redox property of quinones. Three kinds of quinones two electron reduction in buffered acidic solution, unbuffered basic solution, and aprotic solvent, were proposed as shown in Figure 9 in the square. Control of the reduction of ubiquinone and flavin are important in biological systems. The bacterial photosynthetic reaction center provides an extensively studied example. The studies are extended to self-assembly of organic materials. Binding energy and stabilization energy between hydrogen-donor and acceptor altered corresponding to the shape, number, and electron-withdrawing group. V. M. Rotello et al. reported a series of flavins in cooperation with multi-hydrogen bonding. The multi-point hydrogen-bonding stabilized the reduction potential to cause protonation even though strength of a hydrogen-bonding was similar to the single hydrogen-bonding.

![Figure 10](image-url)

**Figure 10.** (a) Ubiquinone binding site of the *Rhodobacter sphaeroides* photo-synthetic reaction center. (b) Ubiquinone and its receptor complex. (c) Organic molecules and hydrogen-bonding

Fukuzumi et al. investigated the correlation ship between hydrogen-bonding and quinone in the view point of photo-induced electron-transfer from electron-donor to
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electron-acceptor where typically ferrocene was employed as electron-donor. The rate constant was increased with metal cation. The report concluded that rigid amide bonding shortened the distance between donor and acceptor. However, there is still no comprehensive explanation for the enhancement of the rate constant.\textsuperscript{44}

1.5 Conductive Carbon Materials

Today, “elemental strategy” is important concern in Japan where is little natural resources. Increasing demand for minor metals in BRICs force us to alter the utilization of precious elements to that of common elements emergently. Achievement of high functionality with common elements was aim for material researcher. Additionally, it was also required to avoid the use of harmful materials which was regulated by “Restriction of Hazardous Substances (RoHs)”, “Registration, Evaluation Authorizatic, and Restriction of Chemicals (REACH)” and “Kyoto Protocol to the United Nations Framework Convention on Climate Change”.

Carbon is attracting elements featured by high conductivity, environmental acceptability, and common elements. The biological abundance of carbon is 18.5%, the second next to oxygen in the human body. Carbon has various isotopes such as graphite, diamond, fullerene, and graphene. The use of carbon is fuel, ink, adsorbent, and conductive additives.

1.5.1 Conductive Additives of the Organic Rechargeable Battery

Redox polymers have no electrical conductivity, which is accelerated by electric field, but propagated charges by diffusion phenomena through self-electron exchange reactions of pendant redox centers. The propagation was accompanied by counterion migration facilitated by amorphous backbone.

Organic rechargeable battery was composed of the polymer and conductive carbon composite electrodes. The conductive carbon imparted electrical conductivity to the electrode. The polymer was grinded down to less than 50 μm and mixed with conductive carbon with polar solvent such as NMP. For conductive carbon, various carbon such as Ketjen black, acetylene black, CMC,\textsuperscript{46} carbon fiber and graphene have been investigated. Especially, vapor phase-grown carbon fiber (VGCF)\textsuperscript{45,47,48} enabled high conductivity in the polymer-rich composite (70 wt%), allowing high redox capacity. However, the conductive carbon that showed no redox capacity could lead no doubt to reduce the redox capacity per total weight.
1.5.2 Dissolution of Carbon Nanotubes

Since the discovery of single-walled carbon nanotubes in 1991, electric and mechanical properties are of interest for various material researchers. Although excellent physical properties are attractive for many fields such as battery, the bundling of nanotubes narrows the range of application. Various solvents were investigated to disperse single-walled carbon nanotubes (SWNTs) by Smalley et al.\textsuperscript{51} 1,2-Dichlorobenzene dispersed SWNTs of less than 1 mg/ml, exfoliating π-π stacking by polarity and aromatic ring.\textsuperscript{55,56} Dispersing SWNTs required ultrasonication. Geckeler et al. reported combination method of ultrasonication and centrifugation that further purified SWNTs removing amorphous carbons, metal catalysts, and graphite.\textsuperscript{52}

![Figure 11. Structure of organic rechargeable battery\textsuperscript{49}](image)

**Table 1** Solubility of SWNTs

<table>
<thead>
<tr>
<th>Solvent</th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>95</td>
</tr>
<tr>
<td>Chloroform</td>
<td>31</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>25</td>
</tr>
<tr>
<td>1-Bromo-2-methylnaphthalene</td>
<td>23</td>
</tr>
<tr>
<td>N-Methylpyrrolidinone</td>
<td>10</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>7.2</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>4.9</td>
</tr>
<tr>
<td>1,2-Dimethylbenzene</td>
<td>4.7</td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.3</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>2.6</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>2.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>—</td>
</tr>
<tr>
<td>1,3-Dimethylbenzene</td>
<td>—</td>
</tr>
<tr>
<td>1,4-Dimethylbenzene</td>
<td>—</td>
</tr>
<tr>
<td>Ethanol</td>
<td>—</td>
</tr>
<tr>
<td>Toluene</td>
<td>—</td>
</tr>
</tbody>
</table>

28
It is essential for dispersion of CNTs to wrap the surface of SWNTs.\textsuperscript{33} There are two strategies using destructive or non-destructive interactions. Covalent-bonding functionalization provided the strongest interaction between wrapping agent and the sp\textsuperscript{2}-carbon surface of SWNTs. Considerable number of reactions such as oxidation, esterification,\textsuperscript{57} 1,3-dipolar cycloaddition,\textsuperscript{58,59} radical reaction and nitrene addition. These chemical reactions were introduced on the side wall of SWNT with alkyl chain and functional moieties. The functionalization methods are destructive to C-C bonds. In contrast,\n
\textbf{Figure 12.} Covalent and non-covalent functionalization of SWNTs.
non-covalent bonding allowed maintaining of high conductivity of pristine SWNTs, spoiling the excellent physical performances. The interactions applied \( \pi-\pi \) stacking,\(^{55} \) polymer wrapping, micellization,\(^{56} \) and \( \pi \)-cation interaction.\(^ {60,61} \) The small molecules surfactant used \( \pi-\pi \) stacking of the aromatic ring such as pyrene and ionic liquid combined with long alkyl chain for solubilization. Polymer wrapping employed various kind of polymers, i.e. DNA, polystyrene, \( \pi \)-conjugated polymer, and water soluble polymer bearing polyethyleneglycol or crown ether. Electrostatic repulsion was also employed to exfoliate each nanotube. The dispersed SWNTs were analyzable by NMR showing shielded effect around SWNTs.\(^ {54} \)

### 1.5.3 Conductive Carbon Nanotube Films\(^ {62} \)

Polymer/nanotube composites offer a simple avenue to reinforce electric, thermal, and mechanical properties of the pristine polymers. One of the important goals in the polymer/carbon nanocomposite fabrication is to enhance the electric properties, while maintaining the high visible transparency of the polymer matrix. In particular, various methods to obtain homogeneous dispersion of carbon nanotubes (CNT) in amorphous and transparent polymers such as poly(methyl methacrylate) (PMMA) are currently challenged to prepare optically transparent and electrically conducting materials as an organic, rare metal-free alternative of ITO.

Carbon nanotubes provide high conductivity to polymer by virtue of conductive pathway. The high aspect ratio of SWNTs allowed forming of percolation threshold of conductive pathway at low weight loading ratio. Conductive polymers have limited thermal and electrical stability, low durability, and relatively poor mechanical properties. These characteristics are very important for transparent applications. So that, carbon nanotubes were expected to exhibit high conductivity. A number of carbon nanotube-based transparent electrodes was prepared (Table 2).

<table>
<thead>
<tr>
<th>Composite material</th>
<th>Resistivity</th>
<th>Nanotube content</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>8 ( \Omega ) ( \gamma )^{1}</td>
<td>–</td>
<td>90%</td>
</tr>
<tr>
<td>SWNT/PA</td>
<td>1 ( \Omega ) ( \text{cm}^{-1} )</td>
<td>8vol%</td>
<td>85%</td>
</tr>
<tr>
<td>SWNT/PEDOT-PSS</td>
<td>3 ( \Omega ) ( \gamma )^{1}</td>
<td>2 wt%</td>
<td>–</td>
</tr>
<tr>
<td>SWNT bucky paper</td>
<td>40 ( \Omega ) ( \gamma )^{1}</td>
<td>100%</td>
<td>70%</td>
</tr>
<tr>
<td>SWNT/coton</td>
<td>20 ( \Omega ) cm(^{-1} )</td>
<td>high</td>
<td>–</td>
</tr>
<tr>
<td>SWNT/cellulose paper</td>
<td>0.53 ( \Omega ) cm(^{-1} )</td>
<td>8.32%</td>
<td>–</td>
</tr>
<tr>
<td>Touch screen</td>
<td>500 ( \Omega ) ( \gamma )^{1}</td>
<td>–</td>
<td>85%</td>
</tr>
</tbody>
</table>

High conductive carbon nanotubes were required for creating the transparent electrode. The high electrical conductivity is associated only with metallic SWNTs, but all of the
available production methods for SWNTs yield mixtures of metallic and semiconducting nanotubes. Moreover, metallic SWNTs generally represent the minority fraction in the mixtures (statistically 1:2 for metallic/semiconducting). Post-production separation of metallic and semiconducting SWNTs has been pursued by a number of research groups. Sun et al. reported selective dispersion of SWNTs with planar aromatic molecules, such as derivatized free-base porphyrin or pyrene with long alkyl chains. The separated metallic SWNTs demonstrated unambiguously the superior performance of metallic SWNTs.
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Chapter 1

Sources 2007, 165, 398-402.


Chapter 2

Electrochemical Property of Anthraquinone Derivatives

2.1 Introduction

A reversible storage of negative charge is required for organic electrode-active materials, especially for those in anodes of organic batteries to undergo redox reactions at negative potentials for maximizing the electromotive force,\(^1,^2\) and for those in cathodes of the \(\text{Li}^+\)ion batteries to accommodate the \(\text{Li}^+\) ion during discharge.\(^3\) However, the redox sites to undergo such “n-type” reaction are relatively sparse,\(^4,^5\) and have been dominated by quinoids,\(^6,^7\) imides,\(^8\) and \(\pi\)-deficient ring molecules.\(^9-^{19}\) Our recent efforts to establish an entirely organic radical batteries have unraveled the electrochemically fully reversible \(1\text{e}^-\) reaction of organic robust radicals such as galvinoxyls\(^{20}\) and nitronyl nitroxides\(^{21, 22}\) to give galvinolates and the aminoxyl anions, respectively. Our principal finding is that polymers even with aliphatic (i.e., non-conjugated) main chains can transport charge with large current densities when their redox capacities became sufficiently large by incorporating these radicals as pendant groups per repeating unit.\(^{23, 24}\) Such properties are based on their capability of accommodating electrolyte cations deep into the amorphous polymer layer and the enhanced electron self-exchange reaction as a result of the ultimate population of the redox sites which amounts to several molars.\(^{25}\) The design concept of the so-called redox-active condensed matter can be viewed as a general strategy to produce new organic anodes required for organic batteries, solar cells, electrochromic devices, sensors, and other “wet-type” devices.\(^{26}\)

In search of the n-type redox sites to bind to the non-conjugated main chain, we focus on anthraquinone (AQ) derivatives based on the following characteristics: (i) the \(2\text{e}^-\) reaction for the ultimate charging (\(\text{AQ} + 2\text{e}^- = \text{AQ}^{2-}\)) that allows the charge storage with the closed-shell system and leads to the inherently large storage density,\(^{27-^{29}}\) (ii) the robustness that withstand high levels of labile atmospheres during the well-known anthraquinone
process for the production of $\text{H}_2\text{O}_2$,30–34 and (iii) the suitable redox potentials in the range of $-0.5$ to $-1$ V versus Ag/AgCl35,36 which is more negative than those of the p-type organic cathode-active materials such as poly(1-oxy-2,2,6,6-tetramethyl-piperidin-4-yl methacrylate) (PTMA) and poly(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl vinyl ether) (PTVE) near $+0.8$ V37–58 and yet sufficiently more positive than that of the Li anode.59–61 A number of anthraquinone polymers have been examined as the electrode-active materials,62–65 but most of them are $\pi$-conjugated and/or main chain-type polymers66–70 rather than those containing anthraquinone pendants, resulting in the lower capacities than their theoretical densities and low rate performances due to the limited mass transfer process through the slab of the rigid and crystalline conjugated polymer layers. Non-conjugated polymers with benzoquinone pendants prepared so far have suffered from the low charge storage capability due to the undesired reactivity of the reduced state especially at the 2,3-positions of the benzenoid ring.71, 72 Herein, we report the excellent charge storage properties of an anthraquinone-functionalized polystyrene 1 (Scheme 1) prepared by the condensation of the anthraquinone-2-carboxylic acid with poly(4-chloromethyl styrene). The ester linkage was characterized by a good affinity to the electrolyte solution which allowed swelling of the polymer to accomplish the reversible charging/discharging processes for $>50$ cycles without degradation, maintaining a capacity comparable to the formula weight-based theoretical redox density of 146 mAh/g. An important aspect of the redox process of 1 is the unprecedented reversible electrochemistry of the anthraquinone sites in aqueous media. Comparison of the charging/discharging behaviors under nonaqueous and aqueous electrolyte conditions gave insight into the nature of the electroneutralization in the polymer layer.

Scheme. 1

2.2 Synthesis of Polystyrene-Bound Anthraquinone

Polymer preparation

The condensation of poly(4-chloromethylstyrene) and a slightly excess amount of anthraquinone-2-carboxylic acid in the presence of DBU proceeded to completion, resulting in a polymer in which all of the pendant group was substituted with the ester linkage to bind
the anthraquinone group (Scheme 2). The presence of the anthraquinone group per repeating unit was suggested by the following observation. The $^1$H NMR signal from the chloromethyl protons at $\delta = 4.51$ ppm (peak a' in Fig. 1a) disappeared upon the condensation, and a new peak appeared at $\delta = 5.23$ ppm (Fig. 1b) which was ascribed to the methylene protons adjacent to the ester linkage. The $^1$H NMR signals from the protons on the polystyrene backbone survived after the condensation, and those from the anthraquinone group appeared at the lower fields (Fig. 1b). The relative intensity of the resonances from the polystyrene backbone and the anthraquinone pendant was in agreement with the structure of 1. An IR peak for the stretching vibration of the C=O bonds in the anthraquinone group ($\nu = 1772$ cm$^{-1}$) was well resolved from that of the ester linkage ($\nu = 1691$ cm$^{-1}$). A reasonable increase in the molecular weight ($M_n$) while maintaining the polydispersity ($M_w/M_n$) upon the incorporation of the anthraquinone group per repeating unit was revealed by the GPC analysis (Experimental Section). The present method of functionalization is characterized by the high efficiency in contrast to that of the previously examined Friedel–Crafts reaction of polystyrene with anthraquinone-2-carbonyl chloride which suffered from the lower degree of substitution of less than 49%.64,65

2.3 Electrochemistry of Polyanthraquinone in Aqueous and Non-Aqueous Medium

2.3.1 Redox Behavior of the Polymer Electrode

A large resistivity of the polystyrene derivatives such as 1 prompted us to examine the
electrochemical properties as a composite layer with a carbon nanofiber (VGCF) and a binder (PVdF). The polymer 1 was coated on the surface of the carbon nanofiber by sufficient grinding of the mixture in NMP. The 1/carbon composite layer was placed on the surface of a glassy carbon plate as a current collector by a solution-based wet process (Experimental Section). Dispersion of the particulate 1 on the nanofiber was supported by a SEM observation (Fig. 2a). The composite layer was immersed into an electrolyte solution for electrochemical measurements (Fig. 2b). The electrolyte was a conventional tetrabutylammonium salt, dissolved in CH$_3$CN. The composite layer prepared via the solution-processing adhered to the surface of the glassy carbon plate without exfoliation into the electrolyte solution.

Anthraquinone possesses stable doubly reduced dianions with properties suitable for

![Image](image_url)
high-density charge storage. Electrode reaction of the 1/carbon layer, typically with a composition of 1/VGCF/PVdF = 1/8/1 (w/w/w), yielded two well separated one-electron reduction waves per anthraquinone group at \([E_{pa}(1) + E_{pc}(1)]/2 = −0.79\) V and \([E_{pa}(2) + E_{pc}(2)]/2 = −1.19\) V versus Ag/AgCl (Fig. 2b). The voltammetric response was ascribed to the redox reaction of the anthraquinone pendants in the polymer, based on the following consideration. Firstly, the redox potentials were in good agreement with those of anthraquinone, which showed electrochemically reversible one-electron waves at −0.95 and −1.48 V versus Ag/AgCl (Fig. 2b). Secondly, no redox response appeared for the carbon composite electrode of poly(4-chloromethylstyrene). The two waves in Fig. 2b were thus ascribed to the successive 1 e\(^−\) reductions of the anthraquinone pendants into the anion radical \((AQ + e^− = AQ^−)\) and the dianion \((AQ^− + e^− = AQ^{2−})\). A set of two resolved reduction processes with small peak-to-peak separations of less than 100 mV was indicative of a multiple, almost non-interacting redox behavior, which allowed one to approximate that electronic interaction between the pendant groups was small and that the anion radical \((AQ^−)\) localized on different sites in the radical polyanion. The redox capacity for the 1/carbon composite determined by the integration of the voltammogram in Fig. 2b was comparable to the number of the anthraquinone groups present in the composite layer (vide infra). The absence of the diffusion tail indicated the fast electrode kinetics and the mass-transfer process for the redox reaction of the anthraquinone groups. The voltammogram persisted without change for continuous charging/discharging cycling in CH\(_3\)CN, in which the composite layer appeared swellable but insoluble. It may be noted that the cyclic voltammograms in Fig. 2b were recorded in an open electrochemical cell by purging argon. This stability and redox cyclability is relatively high and uncommon compared to that of n-dopable conjugated polymers which generally lose their electroactivity after several potential scans because of the high reactivity of the radical polyanions to ambient exposure. The redox cyclability of the 1/carbon layer was even better than those reported for the n-type redox polymers such as poly(nitroxylstyrene),\(^{73}\) suggesting the improvement of the stability and inertness of the reduced or charged state.

The dynamics of ionic species in the layer gave insight into the processes responsible for the charging/discharging behavior. The origin of the ion dynamics for the charge neutralization is associated with the redox gradient-driven charge transport across the polymer layer (vide infra). Electroneutrality requires that the addition of each electron to the polymer layer result in the insertion of one electrolyte cation into the layer. The charge transport across the electrically nonconductive polymer layer is accomplished by electron hopping between the highly populated redox-active anthraquinone groups. Our previous studies revealed that redox sites with large heterogeneous rate constants for electrode reactions, such as TEMPO in the order of \(k_0 = 10^{−1}\) cm sec\(^{−1}\), are likely to undergo outer-sphere electron self-exchange reactions to allow efficient redox gradient-driven
charge transport when they are densely populated in the polymer layer with a small site-to-site distance $\delta$ of $\sim 10 \text{ Å}$.\textsuperscript{23–25} The Nicholson plots of the peak-to-peak separation versus the scan rate in cyclic voltammetry revealed a relatively large rate constant for anthraquinone ($k_0 = 2.2 \times 10^{-2} \text{ cm sec}^{-1}$ in CH$_2$Cl$_2$). Although evaluation of the diffusion coefficient for the propagating charge within the polymer layer was not accomplished due to the absence of reliable data for the thickness of the swollen polymer layer, the rate constant for the electrode reaction of the anthraquinone sites and their high density (e.g. $\delta = 8.5 \text{ Å}$ calculated for 1 based on the formula weight assuming a density of 1 g/cm$^3$) suggested the outer-sphere mechanism to allow efficient charge transport process similar to those in the radical polymers.\textsuperscript{23–25}

Added support for the negative charging of 1 per repeating unit was provided by examining the electrochemistry of the carbon composite in an aqueous electrolyte. The advantage of the aqueous electrolyte is the capability of employing strongly basic conditions which is sufficient to stabilize the benzenoid dianion. However, the lack of solubility of anthraquinone in H$_2$O has impeded the studies on the aqueous electrochemistry. An intriguing aspect of 1 is that it undergoes homogeneous swelling even in H$_2$O to allow almost all of the anthraquinone pendants fully accessible for the electrode reaction and the bimolecular redox reaction. The cyclic voltammogram of the 1/carbon composite electrode showed a single reversible response under the aqueous and strongly basic conditions (Fig. 2c), in contrast to the stepwise waves obtained for the nonaqueous conditions. The redox wave in Fig. 2c was ascribed to the 2e$^{-}$ reduction of the anthraquinone pendants to the dianion (AQ + 2e$^{-}$ = AQ$^{2-}$), based on the amount of the integrated charge which exceeded the theoretical capacity of 73 mAh/g for the 1e$^{-}$ reaction (vide infra), and the absence of any response at potentials more negative than $-1.2 \text{ V}$ versus Ag/AgCl. The one-step reduction to the dianion suggested the enhanced stability of the dianion over the radical anion, and is reminiscent of the strong interaction of the phenolate oxygen with H$_2$O through hydrogen bonding which was previously reported for the aqueous electrochemistry of benzoquinone derivatives under the basic conditions.\textsuperscript{2, 75} These redox behaviors suggested the usefulness of 1 as the electrode-active material in aqueous rechargeable devices.

2.3.2 Charging/discharging behaviors

The galvanostatic $E$–$t$ curves showed plateau regions which agreed with the redox potentials of the polymer. The amount of charge consumed during the galvanostatic electrolysis (Fig. 3a) coincided with ca. 60% of the formula weight-based capacity, which revealed that a large amount of the sites in the layers underwent the redox reaction. The 0.40 V separation between $[E_{pa}(1) + E_{pc}(1)]/2$ and $[E_{pa}(2) + E_{pc}(2)]/2$ under the nonaqueous conditions (Fig. 2b) permitted bulk reduction to be carried out in two discrete steps (Fig. 3a). The integrated charge of 94 mAh/g under the aqueous conditions (Fig. 3a) was ca. 65% of
the theoretical $2e^-$ capacity. Note that these capacities are the intrinsic values of the polymers without consideration of the incorporated ions in the charged state. The mass-specific capacity has been calculated based on the weight of the polymer in the carbon composite, so that the overall capacity of the composite electrode depends on the polymer content. Increasing the content of the polymer resulted in a lowering of the redox activity, due probably to the decrease in the dispersity of the polymer at the carbon nanofiber surface. However, as a consequence of the relatively large redox capacities and the negative redox potentials, the I/carbon composite electrode has the potential opportunity for use as the organic anode-active material.

Figure 3. (a) Galvanostatic chronopotentiogram for the charging and discharging of the I/carbon composite electrode electrolyzed at 0.2 mA. The electrolytes were an CH$_3$CN solution of 0.1 M TBAClO$_4$ (dashed curve) or an aqueous solution of 0.1 M NaCl at pH = 13 (solid curve). Other conditions were as in Fig. 2. (b) Rate performance for discharging of the I/carbon composite electrode at the rate of 3, 37, and 75 C with the descending order of the capacity. The electrolyte was an aqueous solution of 0.1 M NaCl at pH = 13.

It may be noted that the I/carbon composite exhibited a strikingly high current capability, allowing rapid discharging within 1 min and large discharging currents (i.e. 75 C rate (Fig. 3b), where the 1 C rate is defined as the current density at which the discharging of the electrode takes 1 hr) without substantial deviation of the plateau potential. This property is attributable to the rapid electrode reaction of the anthraquinone pendants and the efficient charge propagation throughout the polymer layer. Such a rapid redox process of the polymer electrode suggested the rapid incorporation and release of the charge-neutralizing cation (Na$^+$) which can be ascribed to the amorphous nature of the polymer, in contrast to the slow lithium-insertion process of the conventional cathode in the Li ion battery.

Cyclic performance of the nanocomposite electrode was examined by repeated charging–discharging galvanostatic cycles, which revealed that the redox capacity converged on ca. 80–85% of the initial capacity after several cycles due probably to a partial dissolution of the polymers into electrolyte solution (Fig. 4), but that the converged
capacity exhibited excellent cyclability up to 50 charging/discharging cycles without further degradation. The initial slight increase in the capacity is most likely the swelling process of the polymer in H$_2$O.

Figure 4. Cycle performance of the I/carbon composite electrode for the repeated charging/discharging process in the aqueous electrolyte. The capacity obtained for the discharging process is plotted every 5 cycles. The capacity reached the maximum at 62 mAh/g after charging/discharging for 5 times, which was set at 100% of the relative capacity.

Sandwiching an aqueous electrolyte layer with a couple of redox polymers which are different in potentials provide a charge storage device. We preliminarily fabricated a cell using the composites of I/carbon and PTVE/carbon composites as the anode- and the cathode-active materials, respectively, using a separator film. The fabricated totally organic secondary battery showed a charging/discharging cyclability. The charging process corresponded to the oxidation of the nitroxide radicals in PTMA to the oxoammonium cation at the cathode$^{52-58}$ and the reduction of the anthraquinone groups in I to the anion radical at the anode. The electromotive force of the cell corresponded to the potential gap between the two redox couples. The negative redox potential of I gave rise to the large voltage, which was advantageous for high-density energy storage. The cyclic performance during the repeated charging/discharging process was free of significant deterioration in the redox capacity up to 50 cycles. Although the I/carbon electrode showed less negative potential than the Li metal and the Li/carbon electrodes, their redox cyclability and large capacities may find applications similar to or beyond those of widely pursued Li-based anodes, especially to fabricate various types of entirely organic secondary batteries.

Our efforts have been directed toward further increasing the theoretical redox capacity of the anthraquinone electrodes and defining their rate capabilities and temperature dependences. For this purpose, polymers with even smaller formula weights per repeating unit and thus a higher redox site density, in addition to the compatibility to electrolyte solutions, are desired for the efficient charge propagation process within the polymer layer by a site-hopping mechanism. Increasing the content of the polymer in the carbon
composite while maintaining the redox activity, by defining the structural features at the polymer/carbon interface, is expected to increase the substantial charge-storage density of the composite layer.

The anthraquinone-functionalized polystyrene was proposed as a new class of redox polymers with the negative charge storage properties, which was characterized by the redox potentials near −1 V versus Ag/AgCl and the large redox capacity as a result of the capability of using almost all of the redox sites in the polymer. The suitably designed polymer/carbon composite layer on the current collector allowed efficient swelling of the polymer in conventional nonaqueous electrolyte solutions and even in aqueous solutions, which enabled charge propagation and storage by most likely a site-hopping mechanism based on the electron self-exchange reactions within the polymer layer. The use of anthraquinone as the redox sites led to the fabrication of organic anode-active materials with highly cyclable charging/discharging capabilities. The cycle performance persisted for 50 cycles without degradation, which demonstrated the repeatability of the charging/discharging process and the robustness of the anthraquinone pendants.

2.3 Electrochemistry of Polyanthraquinone in Aqueous and Non-Aqueous Medium

2.3.1 Introduction

The organic redox chemistry of quinones is of great interests for playing a key role in considerable area such as bacterial photosynthetic system, enzymatic catalysis and charge-storage materials. Recently we have demonstrated that anthraquinone-substituted polymers showed fast charge-discharge performance as anode-active material attributed to the rapid self-electron exchange reaction between pendant quinone groups. The electron transfer reactions of anthraquinone are important for further improvement of charge-storage property. The electron transfer reaction of anthraquinone could be accelerated by hydrogen-bonding. Redox waves of quinones in cyclic voltammogram showed diminished peak-to-peak separation with addition of hydrogen-bonding donor agent. Linshcitz have systematically studied hydrogen-bonding effect on electrochemistry of quinones in aprotic solvents where quinones underwent two-step 1e− transfer reactions to produce semiquinone radical and dianion, by using quinones and alcohols as hydrogen-acceptor and donor, respectively. The detail investigation revealed that alcohols form more and stronger hydrogen-bondings with dianion Q2− than with semiquinone radical Q−, which caused large positive shift of redox potential of Q−/Q2− reaction. The stabilization was also affected by
concentration of alcohols. The effect of hydrogen-bonding on kinetic aspect has not been investigated.

Quinones undergo stepwise $2e^-$ transfer reaction at negative potential which plays important role as anode-active materials in organic rechargeable batteries. The electron-transfer reactions of quinones proceed cooperating with environmental interactions such as solvent, electrolyte cation, and hydrogen bonding which played important role in biological system where quinones were bound to protein to modulate the electron-transfer process. The interaction of hydrogen bonding expected to offer important effect to anode-active materials showing rapid charging storage. Anthraquinone have been applied with cooperating to pendant groups of aliphatic polymer to demonstrate chemical stability and charge-storage properties at negative potentials as an anode-active material. In the case of cathode-active materials, we have discovered rapid cathode reactions of nitrooxide radical which displayed rapid electron-transfer rate constant between nitrooxide and oxoammonium cation ($k_0 > 10^{-2}$) attributed to independence of covalent bond-formation and breaking. However, anode-reactions represented by anthraquinone were less investigated compared to cathode-reactions in organic rechargeable batteries. The better interpretation of the electron-transfer reaction of anthraquinones interacted with hydrogen bonding provide new insight into rapid electron-transfer reaction as an anode-reaction for higher rate-performance in organic rechargeable battery.

In this section, we report the enhanced rate of electron-transfer reaction of anthraquinone by intramolecular hydrogen bonding in various solvents. AQ, 1-AAQ, 1,4-DAAQ, and 1,5-DAAQ were prepared with amide groups arranged to form intramolecular hydrogen bonding. The formation of intramolecular hydrogen bonding was confirmed by IR-spectra and $^1$H-NMR spectra of NH proton. The dependence of heterogeneous rate constants of the anthraquinones in various solvents was systematically investigated based on the effect of donor number. In addition, we designed and synthesized the polymer PMAQ containing highly populated anthraquinone showing high heterogeneous rate constant due to intramolecular hydrogen bonding. This study offers insight into the role of hydrogen bonding leading to develop anode-active materials for high rate-performance.

\[\text{Scheme 3. Structure of Anthraquinone Derivatives Forming Intramolecular Hydrogen bonding}\]
2.3.2 Anthraquinone Derivatives

FT-IR spectra of 1-AAQ, 1,4-DAAQ, and 1,5-DAAQ quinones was observed at 3204 cm\(^{-1}\), 3198 cm\(^{-1}\), and 3213 cm\(^{-1}\) corresponding to NH stretching vibration (Table 1). \(^1\)H-NMR spectra in CD\(_2\)Cl\(_2\) of 1-AAQ, 1,4-DAAQ, and 1,5-DAAQ showed NH proton at 12.3, 12.5, and 12.2 ppm more downfielded compared to 2-acetoamideanthraquinone (2-AAQ), close to the chemical shift of NH proton reported previously as resonance-assisted hydrogen bonding (Figure 6).

![Figure 6. Chemical structures (a) and \(^1\)H NMR spectra of 1-AAQ (b) and 2-AAQ (c)](image)

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<th>Solvent</th>
<th>(v_{\text{NH}}) (cm(^{-1}))</th>
<th>(\delta) (ppm)</th>
<th>(D_0) (cm(^2)/s)</th>
<th>(k_0) (cm/s)</th>
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*Infrared spectra obtained with KBr pellet. \(^\ast\)The \(^1\)H-NMR chemical shift of N-H proton. \(\dagger\) Experimental conditions: 0.1 M(CH\(_2\)\(_2\))Cl\(_2\), Pt disc as working electrode. Scan rate at 100-2000 mV/s.
2.3.3 Electron-Transfer Reaction of Anthraquinone with Intra- and Inter-molecular Hydrogen bonding

![Cyclic voltammograms](image)

**Figure 5.** Cyclic voltammograms in CH$_2$Cl$_2$ containing 0.1 M (C$_4$H$_9$)$_2$NClO$_4$, scan rate = 100 mV/s, of (a) 1 mM AQ (dashed curve), 1-AAQ (solid curve) and 1,5-DAAQ (solid thick curve), (b) AQ with addition of CH$_3$OH. Inset: $\Delta E = E_{1/2}(1) - E_{1/2}(AQ/AQ)$ (●), $\Delta E = E_{1/2}(2) - E_{1/2}(AQ^2/AQ^2)$ (○) vs (a) the number of hydrogen-bonding, (b) log[CH$_3$OH].

The effects of intramolecular hydrogen bonding on redox chemistry of anthraquinone were investigated using cyclic voltammetry. AQ showed stepwise 2 e$^-$ redox wave at $E_{1/2}(1)$ = -0.98 V and $E_{1/2}(2)$ = -1.47 V. Although the electron-withdrawing property of amide at 2, 3, 6, and 7-position is small, the $E_{1/2}$’s of 1-AAQ and 1,5-DAAQ appeared at positive potential compared to AQ (Figure 5). It could suggest that intramolecular hydrogen bonding thermodynamically stabilized the corresponding anion. As shown in Figure 5 inset, the magnitude of stabilization was represented by $E_{1/2}(1)$’s and $E_{1/2}(2)$’s (as compared to $E_{1/2}(1)$ vs. AQ$^+/AQ$ and $E_{1/2}$ vs. AQ$^2+/AQ^2$, respectively) proportional to the number of intramolecular hydrogen bonding. The stabilization was observed in intermolecular hydrogen bonding between anthraquinone and alcohols. Intermolecular hydrogen bonding much less stabilized $E_{1/2}(1)$ than $E_{1/2}(2)$ corresponding to smaller association constant $K_{eq}(1)$ than $K_{eq}(2)$ in Scheme 2, where hydrogen bonding form after electron-transfer. Largely stabilized $E_{1/2}(1)$ in Fig. 1 indicating strong hydrogen bonding formation to neutral carbonyl groups.

\[
Q + e^- \rightarrow Q^- \\
Q^- + nROH \rightleftharpoons Q^-(ROH)_n \quad K_{eq}(1) \\
Q^-(ROH)_n + e^- \rightarrow Q^2-(ROH)_n \\
Q^2-(ROH)_n + (m-n)ROH \rightleftharpoons Q^2-(ROH)_m \quad K_{eq}(2)
\]

**Scheme 2** Intermolecular Hydrogen bonding between Quinones and Alcohol
Figure 7. Standard heterogeneous rate constants $k$ vs. $\Delta G$.

The electron-transfer rate constants of electrode reaction were determined from Nicholson method (Table 1). The redox potentials of anthraquinones were thermodynamically stabilized with a number of hydrogen-bonding. The stabilization energy per one hydrogen-bonding in acetonitrile was 12 kJ/mol, which was consistent with typical strength of NH-O hydrogen-bonding. It is interesting to note that the electron-transfer rate constants of anthraquinones were also linearly increased with a number of intramolecular hydrogen-bonding (Figure 7).

$$\Delta G = -nF\Delta(E-E(AQ))$$

(1)

The solvation energy, reorganization energy, and the electron transfer rate constant according to inadequate Born equation were expressed as below.

$$\Delta G_{solv}^o = \frac{e^2}{8\pi\varepsilon_0\alpha_0} \left( 1 - \frac{1}{\varepsilon_s} \right)$$

(2)

$$\lambda_0 = \frac{e^2}{16\pi\varepsilon_0\alpha_0} \left( \frac{1}{\varepsilon_{sp}} \cdot \frac{1}{\varepsilon_s} \right)$$

(3)

$$k_0 = Z_ex \exp \left( -\frac{\lambda_0}{4RT} \right)$$

(4)

In the case of acetonitrile,

$$\log k_0 = \log Z_{ex} - 0.024 \Delta G_{solv}^o$$

(5)

In the case of dichloromethane

$$\log k_0 = \log Z_{ex} - 0.019 \Delta G_{solv}^o$$

(6)

Linear regression gave 0.027 kJ/mol for the slope with a standard deviation 0.003 kJ/mol. This result was 10% higher than the prediction of eq 5 which appears to be reasonable.
agreement in view of the approximations required in the derivation. This treatment provided a simple conceptual link between measured electron-transfer rate constant and measured solvation energies which should be of value in the consideration of the factors at work in governing the rates of solution-phase electron-transfer reactions.

In addition intramolecular hydrogen bonding enhanced reversibility of redox. The redox wave of AQ showed the smaller anodic peak current than the cathodic \(i_{pa2}/i_{pc2} = 0.45\) at \(E_{1/2}(2)\). The cathodic peak current and the anodic was almost equal \(i_{pa2}/i_{pc2} = 1.05\) in 1-AAQ, implying that intramolecular hydrogen bonding prevented undesired chemical reaction of anion radical. Smaller peak-to-peak separation at \(E_{1/2}(2)\) for 1-AAQ and 1,5-DAAQ than that for AQ might indicate rapid electron-transfer promoted by hydrogen bonding.

\[
\begin{align*}
Q & \rightleftharpoons E_{1/2}(1) \\
Q^- & \rightleftharpoons E_{1/2}(2)
\end{align*}
\]

\[\Delta E_{1/2} = E_{1/2}(1) - E_{1/2}(2)\] (7)

The interaction between anthraquinones and intramolecular hydrogen bonding was assessed by using difference in formal potentials \(\Delta E_{1/2} (= E_{1/2}(1) - E_{1/2}(2))\) in solvents with various donor number (DN) (Fig. 6). Geiger et al. argued that \(\Delta E_{1/2}\) may increase when the electroneutralization effect was weakened by solvation of positively charged ion. It is noted that tetrabutylammonium cation was employed as weak interacting cation to evaluate the effect of hydrogen bonding.\(^{xx}\) There is a linear relation dependence of \(\Delta E_{1/2}\) on DN. More strongly donating solvents provided greater values of \(\Delta E_{1/2}\) which was remarkable in 1,5-DAAQ. In dichloromethane with small DN (= 2.6), \(\Delta E_{1/2}\) illustrated that the electroneutralization is strongest with 1,5-DAAQ, weaker with 1-AAQ, and weakest with AQ. On the other hand, use of DMF with large donor number provided larger \(\Delta E_{1/2} (>0.55\) V) of all anthraquinones resulting to reduce the deference between \(\Delta E_{1/2}\’s\) among the anthraquinones. The fact indicates that the electrolyte solvated not only electrolyte cation but also proton donated from amide group to prevent electroneutralization, which caused large electron repulsion between negative charges on the anthraquinone derivatives to provide large \(\Delta E_{1/2}\). The chemical shift of NH proton in \(^1H\)-NMR spectra showed upper field shift with higher donor number, implying that donating solvents enhanced shielding effect on NH proton.

2.3.4 Polymerization of MAQ

The poly(N-(9,10-anthraquinone-1-yl)-methacrylamide) PMAQ with the formula weight-based capacity of 184 mAh/g containing 1-AAQ moiety as redox sites were designed and synthesized according to Scheme 3. The monomer N-(9,10-anthraquinone-1-yl)-methacrylamide was synthesized as previously reported with 48
some modification.

Scheme 4 Synthesis of PMAQ

Figure 4. (a) Cyclic voltammogram for the composite electrode of PMAQ in acetonitrile containing 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ at 10 mV/s. The polymer layer was prepared on an ITO/glass plate.

The polymer PMAQ mixed with VGCF and PVdF in N-methyl-2-pyrrolidone (NMP). The obtained slurry was pasted on aluminum foil and dried under vacuum at 40 °C to provide the composite electrode. The cyclic voltammogram of the electrode was shown in Fig. 4. The redox waves appeared at -0.89 and -1.31 V where the cathodic current was equivalent to the anodic current corresponding to 1-AAQ. The capacity was estimated from integrated charge amount of the cyclic voltammogram to show 143 mAh/g (77% of the theoretical capacity). The cycle performance of charging/discharging was investigated using chronopotentiometry (Fig. 4b inset). The electrode retained 44% of the capacity for 100 cycles of charging/discharging at 7.2 A/g (40 C rate, where 1 C is a normalized unit of current density equal to 184 mA/g), allowing discharging within 100 s without a large voltage-drop. This rapid charging property results from the rapid electrode reaction of 1-AAQ pendants and efficient self-electron exchange reactions through polymer layer allowing invasion of medium electrolyte.

In conclusion, this report has demonstrated that formation of hydrogen bonding between anthraquinone and the NH proton of amide group results in enhancement of the rate of heterogeneous electron-transfer reaction when it was arranged at 1- or 1.5-position. The interaction of hydrogen bonding was controlled by electrolyte medium using donor number. In addition, the polymer bearing highly populated 1-AAQ as a pendant groups with high formula weight-based capacity of 184 mAh/g was synthesized and exhibited the high charging/discharging rate performance. This report focused on the rate of electron-transfer reaction of anthraquinone cooperated with intramolecular hydrogen bonding and electrolyte
medium to accomplish high power density. PMAQ showed rapid charging/discharging performance attributed to their rapid electron-transfer reaction and flexible polymer. Further investigation to synthesize polymers for developing anode-active materials is required.

2.5 Experimental Section

Materials
All solvents were purified by distillation prior to use. A vapor-grown carbon nanofiber (VGCF) was obtained from Showa Denko Co. A binder powder, polyvinylidenefluoride (PVdF) resin (KF polymer) was purchased from Kureha Chemical Co. Electrochemical grade tetrabutylammonium perchlorate (TBAClO₄) and sodium chloride (NaCl) were obtained from Tokyo Kasei Co. and purified by recrystallization. 4-Chloromethylstyrene and 2,2′-azobisisobutyronitrile (AIBN) were obtained from Wako Co. Poly(4-chloromethylstyrene) was prepared by the polymerization of 4-chloromethylstyrene with AIBN in THF in the usual manner. All other regents were obtained from Kanto Chemical Co. or Tokyo Kasei Co. and were used without further purification.

Electrode preparation
The polymer PMAQ/carbon nanocomposite electrode was prepared by coating ca. 2 mg of a slurry of PMAQ (10 mg), VGCF (80 mg), and PVdF (10 mg) in NMP (2 ml) on a glassy carbon plate as a current collector (A = 5.0 cm²) and allowing NMP to evaporate at 40°C under vacuum for 12 hr to give the composite layer with a composition of 1/VGCF/PVdF = 1/8/1 (w/w/w).

Electrochemical measurements
Electrochemical analyses were carried out in a conventional cell under argon. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/AgCl immersed in a CH₃CN or propylene carbonate solution of the supporting electrolytes (0.1 M). The formal potential of the ferrocene/ferrocenium couple was 0.45 V versus this Ag/AgCl electrode. An ALS 660B electrochemical analyzer was employed to obtain the voltammograms.

Measurements
¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA500 or Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a JASCO FT-IR 410 spectrometer. Molecular weight
measurements were done by gel permeation chromatography using a TOSOH HLC8220 instrument with CHCl₃ or THF as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin–Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample.

**Polymer grafting to poly(4-chloromethylstyrene)**

To a 35.3 ml THF solution of 4-chloromethylstyrene (540 mg) was added 10 mol% AIBN (58 mg) under argon. The resulting solution was kept stirring at 60°C for 24 hr. Pouring the solution into methanol and washing the collected precipitate with methanol gave poly(4-chloromethylstyrene) as a white powder. Yield: 314 mg (58%). GPC (THF, polystyrene standard): $M_n = 4.4 \times 10^3$, $M_w/M_n = 1.2$. IR (KBr, cm⁻¹): 3023 (νC–H), 2928 (νC–H). Anal. Calcd for C₉H₉Cl: C, 70.83; H, 5.94%. Found: C, 70.42; H, 6.02%.

$^1$H NMR (CDCl₃, 600 MHz, ppm, TMS): δ 1.38 (br, CH₂, 2H), 1.69 (br, CH, 1H), 4.51 (br, CH₂, 2H), 6.47 (m, Ph, 2H), 7.03 (m, Ph, 2H). The obtained polymer was soluble in common organic solvents such as THF and CH₂Cl₂ but insoluble in methanol and hexane.

To a 3.3 ml N-methylpyrrolidone (NMP) solution of poly(4-chloromethylstyrene) (100 mg, 655 µmol unit) and anthraquinone-2-carboxylic acid (182 mg, 721 µmol unit) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (108 µl). The resulting mixture was kept stirring at 70°C for 24 hr. Pouring the mixture into methanol followed by washing with methanol/acetone (1:1 in v/v) using the standard Soxhlet procedure gave 1 as a yellow powder (Scheme 2). Yield: 192 mg (80%). GPC (CHCl₃, polystyrene standard): $M_n = 1.7 \times 10^4$, $M_w/M_n = 1.7$. IR (KBr, cm⁻¹): 1691 (νC=O), 1772 (νC=O). Anal. Calcd for C₂₄H₁₆O₄: C, 78.25; H, 4.38%. Found: C, 74.29; H, 4.15%. $^1$H NMR (CDCl₃, 600 MHz, ppm, TMS): δ 1.91 (CH₂, 2H), 2.18 (CH, 1H), 5.23 (CH₂, 2H), 6.54 (Ar, 2H), 7.15 (Ar, 2H), 7.59 (Ar, 2H), 7.99 (Ar, 4H), 8.55 (Ar, 1H). The obtained polymer was soluble in CHCl₃, but insoluble in THF.

PMAQ was synthesized with adding some modification to previous report for component of a yellow toner.

**N-(9,10-anthraquinone-1-yl)-methacrylamide**

To o-dichlorobenzene solution (67 ml) of 1-aminoanthraquinone (1 g) was added sodium carbonate (0.47 g) at 162 °C. To the solution methacryl acid chloride (0.51 g) was added dropwise for 30 min. The mixture was stirred for 2 h at 162 °C. The solution was filtrated and washed with methanol. The filtrate was evaporated and purified by column chromatography with benzene as an eluent followed by recrystallization from benzene to yield the yellow needle crystal (0.52 g). IR (KBr, cm⁻¹): 3204 (1N=H). $^1$H-NMR(CDCl₃, 500MHz, ppm): δ = 2.31 (s, 6H,CH₃), 7.75 (d, 2H, Ar-H), 8.00 (d, 2H, Ar-H), 9.07 (d, 2H, Ar-H), 12.2 (s, 1H, NH); $^{13}$C-NMR(CDCl₃, 125MHz, ppm): δ = 25.8 116.8, 122.5, 126.1,
134.4, 135.9, 141.9, 169.9, 186.5; Mass: \( m/z \) 291 (found), 291.3 (calcd). Anal. Calcd for C\(_{18}\)H\(_{13}\)NO\(_3\); C, 74.22; H, 4.50; N, 4.81%. Found; C, 74.24; H, 5.08; N, 4.25%.

**Poly(N-(9,10-anthraquinone-1-yl)-methacrylamide)**

In a typical experiment, to a 0.1 M THF solution of the monomer was added 1 mol % azobis(isobutynitril) in the glass tube. The mixture was degassed and backfilled with N\(_2\) three times, sealed under N\(_2\) and stirred at 70 °C for 12h. After cooling, THF was added to dissolve the polymer and the solution was poured into methanol. After drying at vacuum oven, the yellow polymer was yielded (51%). GPC (CHCl\(_3\), polystyrene standard): \( M_n = 7.5 \times 10^3 \), \( M_w/M_n = 1.6 \). \(^1\)H-NMR (CDCl\(_3\), 500 MHz, ppm, TMS): \( \delta \) 1.35 (br, 3H, CH\(_3\)), 2.20 (s, 2H, CH\(_2\)), 7.12-7.76 (br, 6H, Ar-H), 8.88 (br, 1H, Ar-H), 9.12 (br, 3H, Ar-H), 12.5 (s, 1H, NH)
References


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Chapter 3

Synthesis of Poly(vinylanthaquinone) for Anode-Active Material in High-Density Charge-Storage Material

3.1 Introduction

Reversible and high-density storage of negative charge is required for an anode-active material in a rechargeable air battery which offers high energy density by employing oxygen in the atmosphere as a cathode-active material. Primary and secondary (or rechargeable) air batteries have been investigated by using various metals. While conventional primary air batteries have been dominated by the Zn/air battery, the rechargeable air battery is still under development because of low cycle performance as a result of the formation of dendrites on the metal anodes. In addition, oxygen reduction catalysts usually require strongly basic or acidic aqueous electrolytes to reduce oxygen at positive potentials, which have limited the materials available for the anodes.

A new strategy to design organic electrode-active materials has emerged recently, based on the discovery of poly(2,2,6,6-tetramethylpiperidin-1-oxy-4-yl methacrylate) as a cathode-active material in rechargeable batteries. Charge storage by the so-called radical battery is accomplished by the ultimate charging of the neutral radical to an oxoammonium cation which is populated on the aliphatic backbone in a large density (ca. $4 \times 10^{-3}$ mol unit/g). The reversible and exhaustive charging of the pendant redox site in a slab of the polymer requires electroneutralization throughout the polymer layer, which is made feasible by employing the swellable backbone to allow facile counterion migration. What has been learned from the studies on the rapid charging/discharging properties of the radical batteries is the capability of the highly populated redox sites to transport charges by successive electron self-exchange reactions driven by redox gradient, giving rise to a large current density of $\sim 0.1$ mA/cm$^2$. The efficient redox mediation has been found for many types of organic robust radical pendants that undergo reversible electrode reactions with heterogeneous electron transfer rate constants in the order of $10^{-1}$ cm/s and large bimolecular rate constants for the exchange reaction in the order of $10^7$ M$^{-1}$s$^{-1}$, by virtue of
the high population and thus of the small site-to-site distance.\textsuperscript{13}

\textbf{Scheme 1} Schematic structure of the rechargeable polymer/air battery.

We anticipated that such an efficient redox mediation should also be found for organic redox-active molecules other than the robust radicals, such as quinones,\textsuperscript{14} imides,\textsuperscript{15} and viologen derivatives,\textsuperscript{10} based on their reversible 2e\textsuperscript{−} redox processes of the pristine benzenoids to give the corresponding quinoids. Especially, anthraquinone have been shown to possess a large heterogeneous rate constant for the electrode reaction (\(>10^{-2}\) cm/s) at a moderately negative potential near \(-0.8\) V\textsuperscript{14} and a noticeable chemical stability among quinones due to the absence of the \(\alpha\)-hydrogen atom which is the most susceptible to degradation. The electrochemical properties suitable for the anode-active materials, together with the particular stability which has been demonstrated from the \(\text{H}_2\text{O}_2\) production process,\textsuperscript{16} prompted us to examine anthraquinone as the pendant group. On the basis of the design principles established in the studies of the radical batteries,\textsuperscript{7,17} we focused on poly(2-vinylanthraquinone) (PVAQ)\textsuperscript{18} in which the 2e\textsuperscript{−} redox sites are directly bound to the aliphatic backbone to maximize the formula weight-based theoretical density (229 mAh/g). While most of the anthraquinone-containing polymers in the previous reports possess \(\pi\)-conjugated backbones designed for semiconductor applications,\textsuperscript{19} studies on the aliphatic polyanthraquinones have been limited by the low molecular weights and the poor solubility or swellability ascribed to the crystallization of the pendant groups during the polymerization.\textsuperscript{20} Indeed, the crystalline domain due to the fused ring moieties which is unequilibrated in electrolyte solutions is undesirable for the charge transport and storage, because it significantly lowers the capacity and the rate performance and leads to exfoliation from the electrode.\textsuperscript{21} Here we report the synthesis of PVAQ with a sufficiently high molecular weight to accomplish both swelling and yet insoluble properties in the electrolyte solution, and the excellent charging/discharging properties of the polymer layer allowing the application to the organic anodes.\textsuperscript{22} The cyclability exceeding 300 exhaustive charging/discharging cycles without loss of the capacity from the formula weight-based
theoretical density in the basic electrolyte conditions allowed fabrication of the first organic rechargeable air battery (Scheme 1), which suggested a new type of charge storage configuration in secondary batteries.

3.2 Synthesis of Poly(2-vinylanthraquinone)

Quinones are carbonyl compounds containing conjugated core which provide a stable redox property between quinoid and benzenoid structure. Therefore, various polymers containing quinone moiety were the targets of n-type redox polymer. However, syntheses of polyanthraquinones were suffering from the low solubility to various organic solvents. Poly(2-vinylanthraquinone) has one of the simplest structures that doesn’t contain any only with aliphatic backbone. Cassidy et al. first reported the synthesis by using radiation-induced polymerization in 1959, but resulted in low degree of polymerization. Substituent modification could offer a high solubility, but it adds the molecular weight per repeating unit and diminishes a charge-density: the goal of this thesis. The sufficient degree of polymerization was aspired to for more than 50 years.

2-Vinylanthraquinone was synthesized by two steps from 2-aminoanthraquinone via the Stille coupling reaction as follows. (Scheme 2.)

**Polymerization of 1** The monomer 1 was polymerized to PVAQ using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Polymers obtained from the reactions in toluene, benzene, and THF were all oligomers due to precipitation in the course of the polymerization. A sufficiently large molecular weight (vide infra) was accomplished by employing 1,2-dichloroethane as the solvent, in which the polymerization proceeded without any precipitation. After the polymerization, the solution was poured into methanol to precipitate the product which was purified by reprecipitation from chloroform to
methanol to yield PVAQ as a light green powder. Yield: 92%. GPC (chloroform eluent, polystyrene standard): $M_w = 7.8 \times 10^4$, $M_w/M_n = 1.6$, Anal. Calcd for C$_{16}$H$_{10}$O$_2$: C, 81.9; H, 4.30%. Found: C, 80.7; H, 4.08%. $^1$H NMR (CDCl$_3$, 600 MHz, ppm, TMS): δ 8.30–7.01 (br, 7H, Ar), 2.88–1.71 (br, 3H). $^{13}$C NMR (CDCl$_3$, 150 MHz, ppm, TMS): δ 183.5–179.0, 152.5–148.8, 134.9–129.7, 128.5–124.3, 45.2–37.8. DSC (10 °C/min, under argon): $T_g = 160$ °C. TG-DTA (10 °C/min, under argon): $T_{d10\%}$ (temperature for 10% weight loss) = 379 °C. Results of the polymerization are summarized in Table 1.

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>[AIBN]/[I]</th>
<th>yield(%)</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>1.2-dichloroethane</td>
<td>0.01</td>
<td>83</td>
<td>$7.8 \times 10^4$</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
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<td>69</td>
<td>$3.8 \times 10^4$</td>
<td>1.7</td>
</tr>
<tr>
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<td>90</td>
<td>$8.1 \times 10^3$</td>
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</tr>
<tr>
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<td>$6.2 \times 10^3$</td>
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</tr>
<tr>
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<td>67</td>
<td>$6.3 \times 10^3$</td>
<td>2.3</td>
</tr>
</tbody>
</table>

*Determined by GPC with CHCl$_3$.

### 3.3 Aqueous Electrochemistry of Poly(2-vinylantraquinone)

![Figure 1](image)

**Figure 1.** (a) Cyclic voltammograms of PVAQ in 0.1 M aqueous NaCl at pH 8.9 (red), 10.4 (green), 11.8 (blue), and 13.7 (black) at scan rate of 10 mV/s. The pH values were controlled by 2.5 M NaCl and NaOH electrolyte. (b) Dependence of $E_{1/2}$ and redox capacity on the pH value. The redox capacity was calculated from the integrated area of the cyclic voltammograms.

A CHCl$_3$ solution of PVAQ was dropcast on electrode and dried under the solvent vapor to form a thin layer of PVAQ. Effect of pH on the cyclic voltammogram of the polymer layer is illustrated in Figure 1a. The cyclic voltammogram was examined on a same layer by varying the pH of the bathing electrolyte. Under weakly basic conditions near pH 8, the
cyclic voltammogram showed a single redox couple at $E_{1/2} = -0.65$ V, but the peak current and the redox capacity determined by integrating the redox waves were less than 10% of the theoretical density, suggesting low swellability of the layer due probably to the strong $\pi-\pi$ stacking of the pendant group in the aqueous electrolyte. On the other hand, all of the anthraquinonyl pendants underwent the redox reaction at pH 13.7. The negative shift of $E_{1/2}$ with increasing the pH (Figure 1b) indicated the destabilization of the reduced polyanion under the basic conditions with a rough magnitude of $\Delta G = -nF\Delta E = 16$ kJ/mol. At pH 13.7, the integrated redox capacity was equal to the formula weight-based density, and a highly reversible charging/discharging cycle was accomplished. Plots of the relative capacity versus the pH of the electrolyte revealed the presence of two sudden increases in the capacity at pH 9.5 and 12.1 (Figure 1b), which agreed well with the protonation constants $pK_{a1}$ and $pK_{a2}$ for anthraquinone expressed by eqs 1 and 2.

\[
\begin{align*}
AQH_2 & \rightarrow AQH^- + H^+ & K_{a1} \\
AQH^- & \rightarrow AQ^{2-} + H^+ & K_{a2}
\end{align*}
\]

Smith et al. reported that the reduced state of anthraquinone produced by the overall $2e^-$ reaction ($AQ^{2-}$) exists as an equilibrated mixture of the dianion $AQ^{2-}$, the protonated anion $AQH^-$, and hydroanthraquinone $AQH_2$ and that their distribution depended on the $pK_a$ of water/ethanol and the total concentration of the species.\(^{23}\) In electrolytes at the pH below $pK_{a2}$, the species should be dominated by $AQH^-$ and $AQH_2$, resulting in the low swellability and the poor redox properties due to the strong hydrogen-bonding interaction between the pendant groups. At the pH larger than $pK_{a2}$, $AQ^{2-}$ becomes the major species which is free from the intersite interaction. Based on the reported values of $pK_{a1} = 9$ and $pK_{a2} = 12.05$ for the eqs 1 and 2,\(^{22c}\) the fully reduced state of anthraquinone at pH 13.7 should be composed of $97.8\%$ of $AQ^{2-}$, $2.2\%$ of $AQH^-$, and $0.0\%$ of $AQH_2$.\(^{23}\) While the backbone of the polymer was still insoluble in the aqueous electrolyte, the anionic pendant groups underwent swelling to accommodate H$_2$O and counterions to allow the exhaustive charging/discharging cycle.

Dependence of $E_{1/2}$ on pH provided added support for the interpretation of the redox activity of the PVAQ layer. Plots of $E_{1/2}$ versus pH in Figure 1b obtained under strongly basic conditions (pH $> 12.1$) revealed the negative redox potential near $E_{1/2} = -0.82$ V. In the range of $9.5 < pH < 12.1$, $E_{1/2}$ shifted positively with a slope of $-54$ mV/pH. At pH less than 9.5, $E_{1/2}$ was almost constant near $-0.65$ V, which suggested the slow kinetics of the protonation in the polymer compared to the electrode reaction. The constantly narrow peak-to-peak separation (75–190 mV) in the range of pH 9.6–13.7 in Figure 1a compared to the case of hydroquinone (>300 mV) revealed the rapid self-exchange reactions between the pendant groups which was independent of the protonation equilibrium.
Synthesis of Poly(vinylanthraquinone) for Anode-Active Material in High-Density Charge-Storage Material

Figure 2. Behaviors of the PVAQ layer on the glassy carbon QCM electrode shown by the resonant frequency change during the redox cycling. The electrode potential was scanned between -0.4 V and -1.4 V at scan rate of 10 mV/s in (a) 0.1 M NaOH at pH 12.6 (blue), (b) 0.1 M NaCl at pH 8.2 (red), and (c) 1 M NaCl at pH 8.2 (black).

Figure 3. Cross-sectional SEM images of the PVAQ layer on GC electrodes before (a, b) and after (c) voltammetric experiment. Scale bar: (a) 3 μm, (b) 200nm, and (c) 200nm.

A PVAQ solution in CHCl₃ was dropcast under the solvent vapor and dried to form a layer with a thickness of 140 nm on a glassy carbon QCM electrode (the diameter \( \phi = 0.5 \) cm). Change in the resonant frequency \( \Delta f \) measured simultaneously with the cyclic voltammograms was recorded in the potential range between -0.4 and -1.4 V, at a scan rate of 10 mVs⁻¹ (Figure 2). The increment of the mass \( \Delta m \) accompanied by the reduction of the polymer layer was determined by employing Sauerbrey’s Equation (3):

\[
\Delta f = -2f_0^2A^{-1}(\rho_q\mu_q)^{1/2}\Delta m
\]  

(3)

Where \( f_0 \), \( A \), \( \rho_q \), and \( \mu_q \) are the fundamental frequency of the QCM (9.1 MHz), the electrode area (0.196 cm²), the density of quartz (2.65 gcm⁻³), and the shear modulus of quartz (2.95×10¹¹ dyncm⁻²), respectively. At pH 12.6, \( \Delta f \) decreased and reverted to its original value during the cyclic voltammetry measurement, indicating the reversible ingress...
and release of the counterion and H₂O. However, the Δm at pH 8.2 was much smaller than that at pH 12.6 (Figure 2a, b) even with higher ionic strength up to 1 M (Figure 2c). The maximum increment per the electrode area Δm/A was 3.9 and 0.12 μg/cm² at pH 12.6 and 8.2, respectively. These results suggested that the redox capability of the PVAQ were dominated by pH, rather than the ionic strength of the electrolyte.

The cross-sectional SEM images of dropcast PVAQ layer on GC electrode before and after the voltammetric experiments were shown in Figure 3. The GC electrode was homogeneously covered with the PVAQ layer of 140 nm thickness. Cyclic voltammetry of the layer was performed in 2.5 M NaOH electrolyte at pH 13.7 for 30 cycles. After the cyclic voltammetry, Figure 3c shows a bumpy surface of PVAQ layer with thickness of 143±5 nm. The pristine shape was maintained with a small volume increase within 4%, indicating that counterions and H₂O were smoothly transferred through the PVAQ layer without elution and deformation of the layer.

Figure 4. Cycle performance of PVAQ for charging (○) and discharging (●) capacity. Inset: charging and discharging curves of PVAQ, in 30 wt % NaOH electrolyte (pH 14) at a current density of 5 A/g with a layer thickness of 80 nm.

The charging/discharging property of the PVAQ layer was investigated in 30 wt% NaOH electrolyte. Figure 4 (inset) demonstrates the presence of a plateau region between –0.75 and –0.85 V obtained for the galvanostatic electrolysis of the PVAQ layer, which coincided with the E₁/₂ of PVAQ in Figure 1a. The reversible charging/discharging capacity of 217 mAh/g was achieved with a 100% Coulomb efficiency, which agreed with the theoretical capacity of 229 mAh/g, indicating that all of the pendant anthraquinone groups underwent the reversible 2e⁻ redox reaction to AQ⁻² without undesired reactions such as electrophilic attack, dimerization, and irreversible binding of electrolyte cations. Cycle performance of the polymer layer (Figure 4) revealed that 91% of the initial capacity was maintained after 300 cycles, which was strikingly robust compared to other n-type redox materials having similar high density (>200 mAh/g) such as π-conjugated and nonconjugated polymers. While the high solubility of the reduced state is usually the
problem for those polymers and the polysulfide analogue, no significant elution of PVAQ was observed during the repeated charging/discharging cycles.

3.4 Preparation and Battery Performance of Polymer/Air Battery

An air battery was fabricated by employing the PVAQ anode and the oxygen cathode placed in a coin-type cell assembly containing a 30 wt % NaOH solution (Figure 5). The linear sweep voltammogram of the cathode showed onset of the O₂ reduction current at −0.1 V. A punched coin-type case (Hosen Co.) was employed as an electrochemical cell. A PVAQ solution in CHCl₃ was dropcast on a disk electrode and dried under the saturated solvent vapor to form a layer, which was put into the case as anode. An oxygen reduction catalyst composed of vapor-grown carbon fiber (Showa Denko Co.), MnO₂, and poly(vinylidene fluoride) (90:5:5 in w/w/w) was molded on a Ni grid, which was placed on a Teflon substrate and employed as cathode. The cell was filled with 30 wt% of NaOH or KOH electrolyte. The schematic structure of the coin-type cell was shown in Figure 3.

The cyclic voltammogram of the cell is shown in Figure 6a (inset). The charging and discharging voltages were 0.92 and 0.63 V corresponding to the potential gap between the anode and the cathode (Figure 6a). The charging curve obtained for the electrolysis at 3 A/g (15 C) showed a plateau voltage near 0.75 V, and the discharging curve at the same current density appeared near 0.5 V with the Coulomb efficiency of 91% (Figure 6a), demonstrating the reversible charge storage property of the cell. The rate performance of the discharging process is shown in Figure 6a. The cell exhibited a small voltage drop but kept the discharging capacity of 214 mAh/g which was 93% of the theoretical capacity even at a
Figure 6. (a) Charging and discharging curves of a PVAQ/air cell at various discharging rates of 3, 7, 10, 14, 20, 27, and 34 A/g (15—300 C) in 30 wt% KOH electrolyte. The PVAQ layer was 30 nm in thickness. Inset: cyclic voltammogram of the cell at a scan rate of 5 mV s⁻¹. (b) Cycle performance of PVAQ for discharging (●) capacity at a current density of 15 A/g.

Rapid discharging of 34 A/g (150 C) which corresponded to the full discharging within 24 s. The discharging capacity was maintained for 500 cycles (Figure 6b, Supporting Information). It may be noted that once the electrolyte was degassed by argon before the fabrication process, the cell operated without additional supply of O₂ during 500 cycles, which suggested the possibility of fabricating air batteries in a closed system. Exposure of the cell to O₂ always brings about the unfavorable possibility of the autoxidation of the reduced polyanion through the cathode, so that one usually has to consider the use of O₂-blocking electrolyte layer. The preliminarily established mass balance for AQ⁻² with the amount of O₂, which is produced by the oxidation of OH⁻ during the initial charging, supported the effectiveness of the test cell (Figure 6b, Supporting Information) which accomplished more than 500 charging/discharging cycles. This stability may also result from the fact that O₂ is sparingly soluble in the aqueous electrolyte and effectively consumed on the hydrophobic surface of the cathode. Exploring the electrode configuration to optimize the cell performance is the topic of our continuous investigation.

3.5 Experimental Section

Electrochemical Measurements

Electrochemical measurements were performed using an ALS electrochemical analyzer Model 660D. All measurements were performed under an atmosphere of dry argon. A one-component cell with a glassy carbon plate electrode, a platinum wire and a Ag/AgCl electrode as the working, the counter and the reference electrodes, respectively, were employed to obtain the voltammograms. Aqueous electrolytes were prepared using
deionized water after distillation. The electrolytes at various pH values from pH 13.7 to pH 8.9 were prepared using 2.5 M NaOH and NaCl electrolyte which was thoroughly degassed by argon bubbling. The pH was monitored using a HORIBA F-51 pH meter. Effect of pH on the cyclic voltammograms of the polymer layer was examined by varying the pH of the bathing electrolyte. The formula weight-based theoretical density (or capacity) (in mAh/g) was calculated according to 1000 nFM⁻¹ (3600)⁻¹, where n, F, and M are stoichiometric number of electrons, the Faraday constant, and the molar mass of the repeating unit, respectively. The redox capacity (in mAh/g) was obtained employing 1000 Qm⁻¹ (3600)⁻¹, where Q and m are charge passed in electrolysis and the loading weight of the anode-active material which was determined by weighing the anode or using the concentration of PVAQ in dropcast solution.

**Materials**

All solvents were purified by distillation prior to use. All reagents were purchased from Kanto Chemical Co. or Tokyo Kasei Co. and were used without further purification.

**2-Iodoanthraquinone (2).** Sulfuric acid (20 g, 20 mmol) and NaNO₂ (5 g, 72 mmol) were slowly added to 2-aminoanthraquinone (5 g, 22 mmol) which was stirred for 2 h at 0 °C. The mixture was poured into ice–water (1 L) and stirred for further 1 h. The resulting mixture was filtered, and KI (2.5 g, 15 mmol) was added to the filtrate which was left for 3 h at room temperature. After removal of the precipitate by filtration, KI (2.5 g, 15 mmol) was added again to the filtrate. This operation was repeated until the total amount of the added KI reached 12.5 g. All of the collected precipitate was purified by silica gel column chromatography using CH₂Cl₂ as an eluent to yield 2(2.6 g). FAB-MS (m/z): M⁺ 334.0. Found 335. IR (KBr, cm⁻¹): 1H NMR (CDCl₃, 600 MHz, ppm, TMS): δ 7.81 (t, 1H), 7.82 (t, 1H), 7.99 (d, 1H), 8.15 (d, 1H), 8.30 (m, 2H), 8.65 (d, 1H).

**2-Vinylanthraquinone (1).** To a strictly dried vessel purged with pure argon were purged 2 (201 mg, 0.60 mmol), 2,6-di-tert-butyl-p-cresol (1.02 mg, 4.6 μmol), and Pd(PPh₃)₄ (32.2 mg, 28 μmol). Anhydrous benzene (4.65 mL) and tri-n-butylvinlytin (0.46 mg, 1.9 mmol) were added via syringe to the mixture under argon. The resulting mixture was stirred at 80 °C for 14 h. After cooling to room temperature and evaporating the solvent, the mixture was extracted with CH₂Cl₂ and purified by silica gel column chromatography using dichloromethane/hexane (1:1 in v/v) as an eluent. The obtained solid was recrystallized from benzene/methanol to yield a white needle like crystal. Yield: 62%. FAB-MS (m/z): M⁺ 234.2. Found 235. IR (KBr, cm⁻¹): 1676 (νC=O). Anal. Calcd for C₁₆H₁₀O₂: C, 81.9; H, 4.30%. Found: C, 81.9; H, 4.01%. 1H NMR (CDCl₃, 600 MHz, ppm, TMS): δ 5.54 (d, 1H), 6.05 (d, 1H), 6.87 (d, 1H), 7.80 (m, 3H), 8.28 (d, 1H) 8.32 (m, 3H). 13C NMR (CDCl₃, 150
MHz, ppm, TMS): δ 183.2, 182.6, 143.2, 135.4, 134.1, 134.0, 133.8, 133.6, 133.5, 132.5, 131.4, 128.3, 127.8, 127.2, 124.8, 118.4.

Characterization

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL JNM-LA500 or Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a JASCO FT-IR 410 spectrometer using potassium bromide pellets. Molecular weight measurements were done by gel permeation chromatography using TOSOH HLC 8220 instrument with CHCl₃ as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a JMS-SX102A or Shimadzu GCMS-QP5050 spectrometer. Thermal analyses were performed using a Seiko DSC220C and TG/DTA 220 thermal analyzer under nitrogen.
References


Chapter 4

Redox-Active Polyimide/Carbon Nanocomposite Electrodes

4.1 Introduction

Aromatic imides have been used as n-type semiconductors and electron acceptors in many fundamental studies of n-channel transistors, photovoltaic devices, molecular switches, electrochromic or luminescent devices and models for photosynthesis. These molecules have been used in electron-transfer studies because they undergo reversible one-electron reduction at modest potentials to form stable anion radicals localized on the electron deficient rings. Aromatic polyimides are potentially redox-active polymers, based on the capability of reversible electrochemical reduction of phthalimides into the corresponding anion radicals. Thin layers of polyimides on electrodes derived from pyromellitic anhydrides and diamines have been shown to undergo two reversible redox processes involving addition of one and two electrons to give the electronically isolated anion radical and the dianion, respectively, per repeating unit. However, attempts to use polyimides as electrode-active materials have been impeded by the inherent low permeability of charge-neutralizing electrolyte ions in the polymer due to slow and/or small degree of solvent swelling, which is indeed a defining factor of the charge storage applications.

We have been developing an organic “radical battery” characterized by the use of aliphatic or non-conjugated polymers bearing organic robust radical substituents, such as 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and galvinoxyl, taking advantage of their rapid and electrochemically reversible one-electron redox properties. Molecular design of the so-called radical polymers as electrode-active materials is based on the ultimate population of the radical redox sites per repeating unit to maximize the redox capacity, allowing efficient redox gradient-driven charge transport by electron self-exchange reactions within the polymer. Our principal finding in the development of the radical battery is that
a polymer/carbon nanocomposite strategy dramatically improves the charge storage capability of the radical polymer layers.\textsuperscript{12} In fact, the latest prototype of the coin-type radical battery is composed of a TEMPO-substituted polymethacrylate/carbon nanofiber composite as the cathode and Li metal as the anode sandwiching an electrolyte layer, which has accomplished a power density of 5 kW L\textsuperscript{−1} and a charging/discharging cyclability of more than 10\textsuperscript{4} times at 100 mA. Carbon nanofibers contribute to increase the surface area of the current collector, thereby decreasing the diffusional distance of the electrolyte cations during the charging/discharging processes.\textsuperscript{13} However, the development of totally organic batteries has been held back by the limited range of available organic anode-active materials suitable for charge storage at sufficiently negative potentials to maximize the energy density.\textsuperscript{14}

We anticipated that the strategy of using polymer/carbon nanocomposites could be exploited to implement the concept of charge storage by polyimides, based on the reversible electrochemical reduction typically observed at potentials more negative than −0.5 V \textit{vs.} Ag/AgCl.\textsuperscript{5,6} In this report, we focus on the carbon nanocomposites of two polyimides, poly(4,4′-oxydiphthalimido-1,4-phenylene) and poly(pyromellitimido-1,4-phenylene) (2) (Scheme 1). Layers of these polymers on electrode surfaces were almost redox-inactive without the carbon nanofiber. Interestingly, charge retention with these polymers was unsuccessful even in carbon composites prepared by an exhaustive grinding with the carbon nanofiber, despite the established compatibility of polyimides with various nanocarbons,\textsuperscript{15} but a large redox capacity was produced by elaborating solution processing of the corresponding prepolymers, poly(amide-acid):[(4,4′-oxydiphthalic anhydride)-\textit{alt}-(1,4-phenylenediamine)] (3) and poly(amide-acid):[(pyromellitic dianhydride)-\textit{alt}-(1,4-phenylenediamine)] (4), into composites before the imidization. The results provided insight into the nature of the polyimide/carbon fiber interface that dominate the charge-storage capability. It may be added that the robustness of polyimides is advantageous for use as electrode-active materials to suppress degradation and/or elution into electrolyte solutions, which have often been encountered in the case of many organic electrode-active materials.

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Polyimides for reversible n-type redox reactions at negative potentials.}
\end{scheme}
4.2 Preparation of Composites of Polyimide/Carbon Nanocomposite

A large resistivity of 1018 Ω cm and a slow and/or small degree of swelling in conventional electrolyte solutions, typically observed for aromatic polyimides such as 1 and 2, prompted us to examine their electrochemical properties as a composite layer with a carbon nanofiber (VGCF) and a binder (PVdF). The prepolymer 3 was coated on the surface of the carbon nanofiber by sufficient grinding of the mixture in N-methylpyrrolidone. The 3/carbon composite layer was placed on the surface of an ITO/glass plate or a current collector by a solution-based wet process. The polymer was then imidized to 1 by the ring closing dehydration, accomplished by heating the composite layer at elevated temperatures (see Experimental Section). Coating of each nanofiber with the polymer was supported by SEM observation (Figure 1). ATR-IR spectra for the neat film of the polymer and the polymer/carbon nanocomposite layer both revealed the disappearance of the CO stretching band of the carboxylic acid near 1640 cm\(^{-1}\) accompanied by the heat treatment, and the appearance of new bands near 1705 cm\(^{-1}\) and 1770 cm\(^{-1}\), typically observed for the imide CO vibration (Figure 2).\(^{16}\) The 2/carbon nanocomposite layer was similarly prepared from the 4/carbon layer. Crystallinity of the product provided a support for the imidization. Wide-angle X-ray scattering (WAXS) experiments for the 2/carbon nanocomposite revealed a diffraction peak at 2\(\theta = 21.24^\circ\) (\(d = 4.18\) Å) that corresponded to the intermolecular spacing of the polyimide 2 (Figure 3).\(^{17}\)

Scheme 2. Polyamicacid 3 and 4, the prepolymers of corresponding polyimides 1 and 2.

Figure 1. SEM image of the polyimide 1/carbon nanocomposite electrode.
Chapter 4

Figure 2. ATR-IR spectra obtained for the neat films (a) and the polymer/carbon nanocomposites (b) of the polyimide 1 and the corresponding prepolymer 3.

![ATR-IR spectra](image)

Figure 3. WAXS intensity profiles (CuKa, \( \lambda = 1.5418 \text{ Å} \)) of a mixture of carbon and PVdF (a), 2 (b) and the 2/carbon nanocomposite (c) on a glass substrate. The peak 1 at \( 2\theta = 21.24^\circ \) (\( d = 4.18 \text{ Å} \)) corresponds to the diffraction from polyimide 2. The peak 2 at \( 2\theta = 26 \text{–} 26.30^\circ \) (\( d = 3.385 \text{ Å} \)), overlapped with the broad halo from the glass substrate, is ascribed to the diffraction from carbon.

![WAXS intensity profiles](image)

4.3 Electrochemical Properties of Imides and Polyamides

The nanocomposite layers were immersed into an electrolyte solution for electrochemical measurements. The electrolytes were conventional tetraalkylammonium and alkali metal salts, dissolved in organic solvents such as CH₃CN, DMF and propylene carbonate. The polyimide/carbon layers prepared via the solution processing of the prepolymer 3 and 4 adhered to the surface of the ITO/glass plate without exfoliation into the electrolyte solutions. Electrode reaction of the 1/carbon layer, typically with a composition of 1/VGCF/PVdF = 5/85/10 (w/w/w), yielded a voltammetric wave near \(-1.36 \text{ V} \).
V vs. Ag/AgCl (Figure 4(a)). The voltammetric response was ascribed to the phthalimide/anion radical redox couple in the polymer, based on the following observations. Firstly, the potential was in good agreement with that of the N-methylphthalimide/anion radical redox couple at −1.35 V. Secondly, no redox response appeared before the imidization, as shown by the dashed curve in Figure 4(a). Thirdly, electrolytic in situ ESR spectroscopy recorded for the 1/carbon layer revealed a unimodal signal at $g = 2.004$, which increased in intensity with sweeping the electrode potential to the negative side (Figure 5(a)). The $g$ value was in agreement with that of phthalimide (2.0044). The featureless absorption without hyperfine structures reflected a locally high density of the unpaired electrons on the polymer. It may be added that the ESR spectra persisted under open circuit conditions, due to the durability of the anion radical in the electrolyte solution.

**Figure 4.** Cyclic voltammograms obtained for the polyimide 1/carbon nanocomposite electrodes (solid curves). The electrolyte was a solution of 0.1 M TBAClO$_4$ (a), TBAPF$_6$ (b), TEAClO$_4$ (c), KPF$_6$ (d), NaPF$_6$ (e) and LiPF$_6$ (f) in CH$_3$CN. Scan rate = 10 mV s$^{-1}$. The nanocomposite electrode was prepared by coating slurry of 3, VGCF and PVdF in NMP on an ITO plate and allowing the NMP to evaporate to give the polyamic acid/carbon composite layer; imidization was accomplished by heating the composite electrode (see Experimental Section). Dashed curve in (a) corresponds to a voltammogram obtained for the polyamic acid/carbon composite electrode (i.e. before the imidization).
capacity determined by the integration of the voltammogram in Figure 4(a) was comparable to the number of the imide groups present in the polymer/carbon nanocomposite layer. The absence of the diffusion tail indicated the fast electrode kinetics for the redox reaction of the phthalimide groups. A single reduction peak and a set of two unresolved oxidation peaks with a small peak-to-peak separation of less than 100 mV was indicative of a multiple, almost noninteracting redox behavior, which allowed one to approximate that electronic interaction between the anion radicals was small and that each localized on different imide groups in the radical polyanion. The voltammogram persisted without change for continuous charging/discharging cycling in CH$_3$CN, in which the polymer/carbon nanocomposite layer appeared swellable but insoluble. It may be noted that the cyclic performances in Figure 4 and Figure 5 were recorded in an open electrochemical cell by purging with argon. This stability and redox cyclability is relatively high and uncommon compared to that of n-dopable conjugated polymers which generally lose their electroactivity after several potential scans because of the high reactivity of the radical to ambient exposure.$^{7,20}$ The redox cyclability of the 1/carbon layer was even better than those reported for the n-type redox polymers such as poly(nitroxylstyrene),$^{14b}$ suggesting the improvement of the stability and inertness of the reduced or charged state.

The dynamics of ionic species in the layer gave insight into the processes responsible for the charging/discharging behavior. The origin of the ion dynamics is associated with the redox gradient-driven charge transport across the polymer layer (vide infra). Electroneutrality requires that the addition of each electron to the polymer layer result in the insertion of one electrolyte cation into the layer and/or the Donnan exclusion of the counter

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Figure 5. Electrolytic ESR spectra for the 1/carbon (a) and the 2/carbon (b) nanocomposite electrodes in DMF containing 0.1 M TBACIO$_4$, showing the direction of peak intensity changes on applying negative potentials. The nanocomposite electrodes were prepared by coating the Pt coils with the corresponding poly(amide-acid)/carbon composite layers and heating to undergo cyclodehydration (see Experimental Section). The spectra were recorded at electrode potentials of $-1.23$ (curve 1), $-1.33$ (2), $-1.43$ (3), $-1.53$ (4), $-1.63$ (5) and $-1.83$ (6) V vs. Ag/AgCl for the 1/carbon electrode (a), and $-0.3$ (curve 1), $-1.3$ (2) and $-2.0$ (3) V vs. Ag/AgCl for the 2/carbon electrode (b) under anaerobic conditions.
anion. The absence of a significant effect of replacing ClO$_4^-$ with PF$_6^-$ (Figure 4(b)) on the reduction of the neutral polymer layer suggested that anions may not take part in the redox process. Contrary to this observation, the 1/carbon nanocomposite layer showed different characteristics in different electrolyte cations. In particular, peak currents decreased in magnitudes by replacing the tetraalkylammonium cations with the alkali metal ions, and disappeared with the Li$^+$ ion (Figure 4(d)–(f)), which indicated the strong interaction of these cations with the radical polyanion layer to suppress the charge compensation.\textsuperscript{7}

Diimides possess stable doubly reduced dianions with properties suitable for high-density charge storage. The electro- and photochemical properties of some aromatic diimides have been previously reported.\textsuperscript{21} We focused on the polymer 2, based on the smallest formula weight of pyromellitimidie among the aromatic diimides and, hence, on the large theoretical redox capacity. The cyclic voltammogram obtained for the 2/carbon layer showed two well separated one-electron reduction waves per pyromellitimidie group at \((E_{pa}(1) + E_{pc}(1))/2 = -0.76 \text{ V} \) and \((E_{pa}(2) + E_{pc}(2))/2 = -1.34 \text{ V} \) vs. Ag/AgCl (Figure. 6(a)). The redox potentials were in good agreement with those of dimethylpyromellitimide, which showed electrochemically reversible one-electron waves at −0.68 V and −1.38 V vs. Ag/AgCl. The two waves have been ascribed to the reduction into the anion radical and the dianion,\textsuperscript{21} which was supported by the electrolytic in situ ESR spectra (Figure 7). The anion radical was a good chromophore with intense and characteristic visible absorption bands, which aided in their characterization as the charge-storage material in electrolyte solutions. Under anaerobic conditions, electrolysis of dimethylpyromellitimide to the anion radical with absorption maxima at \(\lambda_{\text{max}} = 714 \text{ nm} \) and 648 nm, and to the dianion at \(\lambda_{\text{max}} = 550 \text{ nm} \) and 522 nm was completely reversible, with isosbestic points near 525 nm and 600 nm, respectively (Figure 8). The recovery of the neutral diimide after more than 1 h of

![Figure 6](image-url). (a) Cyclic voltammogram obtained for the polyimide 2/carbon nanocomposite electrode, showing the almost overlapped 100 curves recorded for continuous cycling of the electrode potential. The electrolyte was a solution of 0.1 M TBAClO$_4$ in propylene carbonate. Scan rate = 10 mV s$^{-1}$. The nanocomposite electrode was prepared by coating a slurry of 4, VGCF and PVdF in NMP on an ITO plate and allowing the NMP to evaporate to give the polyamic acid/carbon composite layer, which was imidized by heating (see Experimental Section). (b) Cyclic voltammogram obtained for a 2/carbon composite electrode prepared by a solventless ball milling of 2 (5 mg), VGCF (85 mg) and PVdF (10 mg), showing the direction of the peak current changes on potential cycling.
Figure 7. Electrolytic ESR spectra for 1 mM \(N,N'\)-dimethylpyromellitimide in DMF containing 0.1 M TBAClO\(_4\). The spectra were recorded at electrode potentials of -0.3 (curve 1), -1.3 (2), and -2.0 (3) V vs. Ag/AgCl under anaerobic conditions.

electrolysis at the negative potentials suggested the sufficient persistency of these species. The electrolytic in situ ESR spectra obtained for the 2/carbon nanocomposite layer revealed the appearance of a featureless ESR signal of the paramagnetic radical polyanion accompanied by the electrolytic reduction (curve 2 in Fig. 5(b)), and the subsequent decrease in intensity of the signal by the further reduction to the dianion at more negative potentials. A broad trimodal absorption at the reduced concentration of the anion radical was similarly observed for the 2/carbon composite (curve 3 in Figure 5(b)) and dimethylpyromellitimide (curve 3 in Figure 8).

Figure 8. Electrolytic UV-vis-NIR spectra for 1 mM \(N,N'\)-dimethylpyromellitimide in DMF containing 0.1 M TBAClO\(_4\). The electrode potentials were set at -1.01, -1.11, -1.21, -1.31 and -1.41 V vs. Ag/AgCl with the ascending order of absorbance at 714 nm (solid curves) and at -1.51, -1.61 and -1.71 V vs. Ag/AgCl with the ascending order of absorbance at 648 nm (dotted curves). Dashed curve represent the spectrum obtained from the pristine imide (i.e., before applying the electrode potential).

A straightforward route to the 2/carbon composite by the direct ball milling of 2 and the carbon nanofiber was unsuccessful. Cyclic voltammetry for the resulting material revealed a gradual decrease in the magnitude of the peak current during the redox cycling (Figure 6(b)).
The cyclic voltammogram in Figure 6(a) demonstrated that the redox wave persisted without change, even after 100 cycles. The result suggested the difficulty of dispersing 2 on the carbon nanofiber surface and demonstrated the importance of the in situ imidization for use as the electrode-active material.

4.4 Charge-Storage Performance of the Organic Secondary Batteries

The charge transport across the electrically nonconductive polyimide layer\(^{22}\) is accomplished by electron hopping between the highly populated redox-active imide groups. Our previous studies revealed that redox sites with large heterogeneous rate constants for electrode reactions, such as TEMPO in the order of \(k_0 = 10^{-1} \text{ cm s}^{-1}\), are likely to undergo outer-sphere electron self-exchange reactions to allow efficient redox gradient-driven charge transport when they are densely populated in the polymer layer with a small site-to-site distance \(\delta\) of 10 Å.\(^{9a}\) The Nicholson plots of the peak-to-peak separation versus the scan rate in cyclic voltammetry revealed a relatively large rate constant for \(N\)-methylphthalimide \((k_0 = 4.6 \times 10^{-2} \text{ cm s}^{-1})\) and \(N,N\)-dimethylpyromellitimide \((k_0(1) = 3.0 \times 10^{-2} \text{ cm s}^{-1})\). Although evaluation of diffusion coefficients for the propagating charge within the polymer layers have been impeded by the absence of reliable data for the thickness of the swollen polymer layer, the rate constants for the electrode reaction of the imide sites and their high density (e.g., \(\delta = 6.2\) Å calculated for 2 based on the formula weight assuming a density of 1 g cm\(^{-3}\)) suggested the outer-sphere mechanism to allow efficient charge transport process similar to those in the radical polymers.\(^{10-13}\)

The galvanostatic \(E-t\) curves showed plateau regions which agreed with the redox potentials of the polyimides. Cyclic performance of the nanocomposite electrode was examined by repeated charging–discharging galvanostatic cycles at different current densities, which revealed that the redox capacity converged on ca. 70% of the initial capacity after several cycles, probably due to a partial dissolution of the polymers into electrolyte solutions (Figure 9), but that the converged capacity exhibited excellent cyclability for more than 100 charging–discharging cycles without further degradation. The amount of charge consumed during the potential scan (Figure 4(a) and 6(a)) and the galvanostatic electrolysis (Figure 9) both coincided with ca. 60% of the formula weight-based capacity, which revealed that a large amount of the sites in the layers
Figure 9. Chronopotentiograms obtained for the 1/carbon (a) and the 2/carbon (b) nanocomposite electrodes at 200 μA. Inset: cycle performance of the nanocomposite electrodes shown by the relative redox capacity in % with respect to the initial capacity for charging (open circles) and discharging (closed circles). Dashed lines represent the relative capacity for discharging converged after several potential cycling.

underwent the redox reaction. The 0.58 V separation between \( (E_{pa}(1) + E_{pc}(1))/2 \) and \( (E_{pa}(2) + E_{pc}(2))/2 \) (Figure 6(a)) permitted bulk reduction to be carried out in two discrete steps (Figure 9(b)). The total redox capacity of the electrolyzed nanocomposites of 2 amounted to 111 mAh g\(^{-1}\), which was still much larger than the formula weight-based theoretical capacities of the already existing redox polymers that exhibit negative redox potentials, such as poly(N-4,4-bipyridinium-N-decamethylene dibromide) (59 mAh g\(^{-1}\) at −0.53 V vs. Ag/AgCl).\(^{23}\) Note that these capacities are the intrinsic values of the polymers without consideration of the incorporated ions in the charged state. Indeed, galvanostatic reduction of the 2/carbon layer prepared on a gold disk at the surface of a quartz crystal microbalance (QCM) assembly resulted in an almost linear decrease in the resonance frequency with the electrolysis time (Figure 10), which suggested an increase in the weight of the layer due to the cation incorporation at a constant rate to accomplish the electroneutrality. It may be noted that the mass-specific capacity has been calculated based on the weight of the polymer in the carbon nanocomposite, so that the overall capacity of the nanocomposite electrode depends on the polymer content. Increasing the content of the polymer resulted in a lowering of the redox activity, probably due to the decrease in the dispersivity of the polymer at the carbon nanofiber surface. However, as a consequence of the relatively large redox capacities and the negative redox potentials, the polyimides have the potential opportunity for use as organic anode-active materials.

Sandwiching an electrolyte layer with a couple of redox polymers which are different in potential provides a charge storage device. We fabricated a coin-type cell using 1/carbon and PTMA/carbon\(^{13}\) nanocomposites as the anode- and the cathode-active materials, respectively, using a separator film. The fabricated totally organic secondary battery showed an excellent charging/discharging cyclability. The charging process corresponded to the
Figure 10. Resonance frequency changes (Δf) recorded during the galvanostatic reduction of the 2/carbon layer electrolyzed at 100 μA (a) and the corresponding chronopotentiogram (b). The 2/carbon layer was prepared on a gold disk with an area of A = 0.196 cm² at the surface of the QCM assembly. The supporting electrolyte was 0.1 M TBAClO₄ in propylene carbonate. Dotted line in (a) represented the least-squares fitted line, demonstrating the occurrence of mass transfer at a constant rate during the galvanostatic electrolysis. The sensitive factor in the Sauerbrey equation was Cᵣ = 1.068 Hz/ng. The equivalent weight (Mₑq) or the mass change relative to the redox capacity, formulated by ΔmF/Q where F was the Faraday’s constant, was Mₑq = 138 g/mol, which was slightly smaller than the formula weight of the electrolyte cation (tetrabutylammonium cation: 185 g/mol), suggesting a concurrence of a back diffusion of the electrolyte anion.

oxidation of the nitroxide radicals in PTMA to the oxoammonium cation at the cathode and the reduction of the phthalimide groups in 1 to the anion radical at the anode. Cyclic voltammetry recorded for the PTMA/carbon electrode in the cell with the electrode potential scanned versus the 1/carbon electrode showed a reversible redox couple at 2.11 V, while at an inverted voltage (i.e. −2.11 V) was observed a redox couple of 1 versus the PTMA electrode (Fig. 5). The electromotive force of the cell corresponded to the potential gap between the two redox couples, which amounted to 2.16 V. The negative redox potential of 1 gave rise to a large output voltage over 2 V, which was advantageous for high-density energy storage. The cyclic performance during the repeated charging–discharging process was free of significant deterioration in the redox capacity, even after 100 cycles. Although the polyimide/carbon electrodes showed less negative potentials than the Li metal and the Li/carbon electrodes, their redox cyclability and large capacities may find applications similar to or beyond those of widely pursued Li-based anodes, especially to fabricate various types of totally organic secondary batteries.

Our efforts have been directed toward further increasing the theoretical redox capacity of the polyimide electrodes and defining their rate capabilities and temperature dependencies. For this purpose, polymers with even smaller formula weights per repeating unit and thus a higher redox site density, in addition to the compatibility to electrolyte
solutions, are desired for the efficient charge propagation process within the polymer layer by a site-hopping mechanism. Increasing the content of the polyimides in the carbon nanocomposites while maintaining the redox activity, by defining the structural features at the polyimide/carbon interface, is expected to increase the substantial charge-storage density of the nanocomposite layer, which is also the topic of our continuous investigation.

**Figure 11.** Two-electrode cyclic voltammograms obtained for the 1/carbon anode (solid curve) and the PTMA cathode (dashed curve) in the coin cell fabricated by sandwiching an electrolyte layer of 0.1 M TBAClO$_4$ in CH$_3$CN. The curves correspond to the converged voltammogram obtained after 100 charging–discharging cycles. Potentials were scanned at a rate of 10 mV s$^{-1}$ versus the counterpart electrode of the cell.

Polyimides were proposed as a new class of redox polymers with a charge storage capability, which were characterized by the negative redox potentials near −1.4 V vs. Ag/AgCl and the large redox capacities over 100 mAh g$^{-1}$. The suitably designed polyimide/carbon nanocomposite layers on electrode surfaces allowed efficient swelling of the polymer in conventional electrolyte solutions, which enabled charge propagation and storage, most likely by a site-hopping mechanism based on the electron self-exchange reactions within the polymer layer. The use of polyimides as electroactive materials led to the fabrication of organic anode-active materials with highly cyclable charging–discharging capabilities. The cycle performance of the fabricated organic charge storage device persisted for more than 100 cycles without degradation, which demonstrated the repeatability of the charging–discharging process.
4.5 Experimental Section

Materials

All solvents were purified by distillation prior to use. A vapor-grown carbon nanofiber (VGCF) was obtained from Showa Denko Co. A binder powder, polyvinylidene fluoride (PVdF) resin (KF polymer) was purchased from Kureha Chemical Co. Tetrabutylammonium perchlorate (TBACL(O_4)), tetrabutylammonium hexafluorophosphate (TBAPF_6), tetracyethylammonium perchlorate (TEACL(O_4)), potassium hexafluorophosphate (KPF_6), sodium hexafluorophosphate (NaPF_6), and lithium hexafluorophosphate (LiPF_6) were obtained from Tokyo Kasei Co. and purified by recrystallization. N-Methylphthalimide was obtained from Wako Co. Poly(1-oxo-2,2,6,6-tetramethylpiperidin-4-yl methacrylate) (PTMA) (M_n = 1.6 x 10^4, M_W = 4.7 x 10^4) was synthesized as previously reported. All other reagents were obtained from Kanto Chemical Co. or Tokyo Kasei Co. and were used without further purification. N,N′-Dimethylpyromellitimide was prepared from methylamine and pyromellitic anhydride, according to the conventional methods with slight modifications. Polyamic acids 3 (M_n = 6.5 x 10^3, M_W = 2.2 x 10^4) and 4 (M_n = 2.5 x 10^4, M_W = 7.4 x 10^4) were prepared by polycondensation of 1,4-phenylenediamine and the corresponding anhydrides.

Electrode preparation

The polyimide 1/carbon nanocomposite electrode was prepared by coating ca. 0.6 mg of a slurry of 3 (5.47 mg), VGCF (85 mg), and PVdF (10 mg) in NMP (1 mL) on an ITO plate (A = 0.785 cm^2) and allowing the NMP to evaporate at 40 °C under vacuum for 12 h to give the polyamic acid/carbon composite layer at 20–50 μm in thickness. Cyclodehydration to polyimide was accomplished by stepwise heating of the composite electrode at 160, 200, 230 and 260 °C for 20 min, and finally at 290 °C for 30 min to give the 1/carbon nanocomposite layer with a composition of 1/VGCF/PVdF = 5/85/10 (w/w/w).

The polyimide 2/carbon nanocomposite electrode was similarly prepared by coating ca. 0.6 mg of a slurry of 4 (5.62 mg), VGCF (85 mg), and PVdF (10 mg) in NMP (1 mL) on the ITO plate and allowing NMP to evaporate to give the polyamic acid/carbon composite layer at 20–50 μm in thickness, which was cyclodehydrated to the polyimide by the stepwise heating at 160, 200, 230 and 260 °C for 20 min, and finally at 290 °C for 30 min to give the 2/carbon nanocomposite layer with a composition of 2/VGCF/PVdF = 5/85/10 (w/w/w).

Electrochemical measurements

Electrochemical analyses were carried out in a conventional cell under argon. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/AgCl immersed in a CH_3CN or propylene carbonate solution of the supporting...
electrolytes (0.1 M). The formal potential of the ferrocene/ferrocenium couple was 0.45 V versus this Ag/AgCl electrode. An ALS 660B electrochemical analyzer was employed to obtain the voltammograms. Electrolytic ESR spectrometry was accomplished by using a handmade ESR sample tube equipped with a Pt coil, a Au wire passing through the Pt coil, and the Ag/AgCl as the working, the auxiliary, and the reference electrodes, respectively. Electrolytic UV-vis.-NIR spectra were recorded using a quartz-glass cell with an optical length of 2 mm, equipped with a Pt mesh, a Pt coil, and the Ag/AgCl as the working, the auxiliary, and the reference electrodes, respectively.

**Fabrication and characterization of test cells**

A coin cell was fabricated by sandwiching the electrolyte layer of 0.1 M TBAClO\(_4\) in CH\(_3\)CN with the I/carbon nanocomposite anode and a PTMA /carbon composite cathode with a composition of PTMA/VGCF/PVdF = 5/85/10 (w/w/w), using a separator film (cell guard #2400 from Hohsen Co.) under anaerobic conditions. The amount of the cathode- and the anode-active materials in the cell was adjusted to have equal capacities, based on their formula weights. Cyclic performance of the fabricated cell was examined by repeated charging–discharging galvanostatic cycles at different current densities. The charging–discharging experiments were typically performed at a current density of 10 C, where 1 C represents the current density required for charging or discharging of the cell at 1 h.

**Measurements**

1H and 13C NMR spectra were recorded on a JEOL JNM-LA500 or Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a Jasco FT-IR 410 spectrometer. ATR-IR spectra were obtained using Nicolet 6700 spectrometer. Molecular weight measurements were done by gel permeation chromatography using a TOSOH HLC8220 instrument with CHCl\(_3\) or THF as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a JMS-SX102A or Shimadzu GCMS-QP5050 spectrometer. ESR spectra were recorded using a JEOL JES-TE200 spectrometer with a 100 kHz field modulation frequency and a 0.1 mT width.

**Synthesis of N,N’-dimethylpyromellitimide.** To a solution of methylamine (5.1 mL, 40% in CH\(_3\)OH, ca. 9.8 M) in N,N’-dimethylacetamide (50 mL) were added pyromellitic anhydride (1.09 g). The resulting solution was heated at 160°C under argon for 12 h with constant stirring. After cooling to room temperature, the precipitated crude product was collected by filtration, washed with H\(_2\)O, and purified by column chromatography using
CHCl₃ as an eluent ($R_f = 0.13$) to give N,N'-dimethylpyromellitimide as a colorless powder (Yield: 81%). MS (m/z): calcd for M⁺ 244.2; found 244.0. IR (KBr, cm⁻¹): 3034 (νC-H), 1766 (νC=O), 1701 (νC=O). Anal. Calcd for C₁₂H₈N₂O: C, 59.0; H, 3.3; N, 11.5%. Found: C, 59.2; H, 3.2; N, 11.2%.

1H NMR (CDCl₃, 600 MHz, ppm): δ 3.26 (s, 6H), 8.28 (s, 2H). 13C NMR (CDCl₃, 150 MHz, ppm): δ 166.3, 137.3, 118.1, 24.5.

**Synthesis of poly(amide-acid):[(4,4'-oxydiphthalic anhydride)-alt-(1,4-phenylenediamine)] (3).** 1,4-Phenylenediamine (649 mg) was dissolved in N,N'-dimethylacetamide (12 mL). To this solution was added 4,4'-oxydiphthalic anhydride (1.86 g). The resulting solution was stirred at room temperature for 6 h under argon. The product was precipitated by pouring the resulting mixture into acetone, which was collected by filtration and dried under vacuum to give 3. Yield: 95 wt%. IR (KBr, cm⁻¹): 1661 (νC=O). 1H NMR (DMSO-δ₆, 600 MHz, ppm): δ 7.99-7.17 (10H), 10.33 (2H), 12.75 (2H). GPC (polystyrene standard, eluent: DMF): $M_n = 2.6 \times 10^4$, $M_W = 8.2 \times 10^4$.

**Synthesis of poly(amide-acid):[(pyromellitic dianhydride)-alt-(1,4-phenylenediamine)] (4).** 1,4-Phenylenediamine (1.08 g) was dissolved in N,N'-dimethylacetamide (25 mL). To this solution was added pyromellitic anhydride (2.18 g). The resulting solution was stirred at room temperature for 6 h under argon. After the reactions, the product was precipitated by pouring the resulting mixture into acetone and collected by filtration. The polymer was purified by reprecipitation from the N,N'-dimethylacetamide solution into acetone repeatedly. After washing the product with acetone and drying under vacuum, the poly(amic acid) 3 was obtained as a yellow powder. Yield: 85 wt%. IR (KBr, cm⁻¹): 1662 (νC=O). 1H NMR (DMSO-δ₆, 600 MHz, ppm): δ 7.71 (4H), 7.97 (1H), 8.31 (1H), 10.52 (2H), 13.32 (2H). GPC (polystyrene standard, eluent: DMF): $M_n = 2.5 \times 10^4$, $M_W = 7.4 \times 10^4$.

**Synthesis of polyimide:[(4,4'-oxydiphthalic anhydride)-alt-(1,4-phenylenediamine)] (poly(4,4'-oxydiphthalimido-1,4-phenylene)) (1).** A film of 3 on a glass substrate was cast from the N,N'-dimethylacetamide solution. Cyclodehydration was accomplished by a stepwise heating at 160, 200, 230 and 260 oC for 20 min and finally at 290 °C for 30 min to give a dark yellow film of 1, which was insoluble in CHCl₃, THF, DMF and DMSO. IR (KBr, cm⁻¹): 1775 (νC=O), 1720 (νC=O), 1360 (νC=N). Anal. Calcd for C₂₂H₁₀N₂O₅: C, 69.1; H, 2.6; N, 7.3%. Found: C, 68.4; H, 2.7; N, 7.5%.

**Synthesis of polyimide:[(pyromellitic dianhydride)-alt-(1,4-phenylenediamine)] (poly(pyromellitimido-1,4-phenylene)) (2).** A film of 4 on a glass substrate, prepared by casting from the N,N'-dimethylacetamide solution, was similarly converted to polyimide by a stepwise heating at 160, 200, 230, 260 and finally at 290 oC to give a dark yellow film of
2. IR (KBr, cm\(^{-1}\)): 1778 (\(\nu_{\text{C}=\text{O}}\)), 1732 (\(\nu_{\text{C}=\text{O}}\)), 1354 (\(\nu_{\text{C}=\text{N}}\)). Anal. Calcd for C\(_{16}\)H\(_6\)N\(_2\)O\(_4\): C, 66.2; H, 2.1; N, 9.7%. Found: C, 65.8; H, 2.1; N, 9.7%.
References


Chapter 4


Chapter 5

Radical Polymer-Wrapped SWNTs for Transparent Charge-Storage Material

5.1 Introduction

The functionalization of carbon nanotubes (CNTs) has been widely investigated\textsuperscript{1-3} and, especially, in conjunction with redox-active molecules this would lead to potential applications for electronic devices.\textsuperscript{4-5} Attachment of redox molecules on CNTs have been offered by relatively strong interactions such as covalent bonding, $\pi$-$\pi$ interactions, and $\pi$-cation interactions.\textsuperscript{6-8} However, these interactions often require destructive and severe conditions with damage to the CNTs, and/or extra functional groups which interfere with the electrochemical and optical properties of the redox-active sites. An efficient functionalization with a non-destructive interaction is required to maintain the inherent properties of both the CNTs and the redox-active molecules. Polymer wrapping, 3-dimensionally interacting with CNTs by weak interactions, could be one of the best methods for functionalizing CNTs with redox-active molecules.

Scheme 1. Radical Polymer-Wrapped Single-Walled Nanotubes.

Charge-storage materials or electrode-active materials for rechargeable batteries consisted of organics have been developed using redox-active molecules\textsuperscript{9} and polymers.\textsuperscript{10-14} We have been successfully developing the organic radical battery\textsuperscript{10-20} utilizing a series of
synthesized polymers containing redox-active organic radicals fenced by bulky alkyl groups.\textsuperscript{15-18} Typically poly(2,2,6,6-tetramethylpiperidine-1-oxy-4-yl methacrylate) (PTMA) was employed as the organic cathode-active pendant group.\textsuperscript{10} The PTMA ideally consists of the flexible polymethacrylate backbone and the spherical pendant 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) group and could be expected to impart the TEMPO’s specific redox functionality to its CNT nanocomposite (Fig. 1a). In this paper, we describe that PTMA-wrapped single-walled carbon nanotubes (SWNT) provide a high dispersibility of the SWNTs and successfully provide the nanocomposite electrode which displayed both a high electrical conductivity through the SWNT network and a quantitative and remarkably high-rate charge-storage capability while maintaining the high transparency of the nanocomposite.

5.2 Preparation of Radical Polymer-Wrapped Carbon Nanotubes

We focused on SWNTs with a diameter of 1—3 nm and a large surface area. To exfoliate the SWNT bundles without surfactants, which could cause electrical insulating,\textsuperscript{21} the previously developed preparation method using ultrasonication and centrifugation was adopted for the dispersion of SWNTs.\textsuperscript{22,23} In a typical experiment, commercial SWNTs aggregation could be observed further ultrasonication for 10 s at 0°C yielded a homogeneous dispersion. It is worth to note that several seconds of ultrasonication was were ultrasonicated in \textit{o}-dichlorobenzene (DCB) for 45 min at 0°C, and the dispersion was
centrifuged. The supernatant was added to the oxygen-free DCB of PTMA. Although some enough to disperse the aggregated wrapped CNTs while pristine SWNTs required more than 30 min, indicating that the wrapping with PTMA enhanced the dispersibility of SWNTs.

To clarify the wrapping efficiency of the SWNTs, TEM samples were prepared using two kind of grids covered with and without carbon film. Firstly, the dispersion was dropcast and dried on a copper grid covered with carbon film, where both PTMA and SWNTs were placed to provide the over view of PTMA/SWNT composite. The TEM image of the dried PTMA/SWNT composite on the carbon film is shown in Fig. S1. Individualized SWNTs were spread homogeneously in PTMA. As far as we observed, no SWNTs existed apart from the PTMA on the carbon film. The length of the SWNTs ranged from several hundred nanometers to micrometers, which is consistent with previous report on dispersion of SWNTs in DCB.\textsuperscript{22} Secondly, TEM sample of the dispersion was prepared on the copper grid without carbon film, where soluble PTMA was filtered off for the high resolution analysis of the PTMA-wrapped SWNTs. A TEM image of the PTMA-wrapped SWNT shows that wormlike chains of PTMA were adsorbed on the flat surface of the SWNT with a width of 0.65 ± 0.06 nm in Fig. 1c, corresponding to the crystal structure-determined size of the pendant TEMPO group in PTMA (Fig. 1b). The PTMA chain bearing the alternately-aligned pendant groups is shown by the linear and double-stranded image of the PTMA chain along a SWNT (Fig. 1d). It could be stated that the linear conformation of a single vinyl polymer chain with bulky pendant TEMPO groups was visualized via wrapping on a SWNT. The PTMA-wrapped SWNTs were highly individualized in DCB that is consistent with precious reports. The wrapping prevented the aggregation of SWNTs and also made them to be stable for >2 months without precipitation. The composite was dispersible even in chloroform after drying, in which the pristine SWNTs were substantially insoluble, suggesting that the wrapping allowed solvation due to the affinity of the PTMA to the solvents.

![Figure 2](image_url)

**Figure 2.** TEM image of the PTMA/SWNT dispersion dropcast on copper grid covered with carbon film. Scale bar: (a) 500 nm, (b) 100 nm.

The dispersion of PTMA/SWNT was dropcast on a carbon-film-coated copper grid. Both the polymer and SWNTs was held on the carbon film. Fig. 2a shows that a number of
dispersed SWNTs were covered with PTMA. PTMA-wrapped SWNT apart from PTMA matrix was shown in Fig. S1b. It is difficult to obtain a higher magnification of SWNTs on the carbon film because few nano-meter thickness of the carbon film prevented focusing on SWNTs.

The cross-sectional SEM images of PTMA/SWNT composite are shown in Fig. 3. The ITO electrode was homogeneously covered with the PTMA/SWNT layer (2.7 μm). A magnified image of the electrode in Fig. 3b shows that white spots corresponding to cross-sectional edges of SWNTs were well scattered in the PTMA. The average distance between each spots was ca. 260 nm obtained from spots number per 4 μm². These highly dispersed SWNTs suggest that SWNT kept individualized during the drying of the composite film at 75 °C, although dispersed SWNTs in DCB tend to aggregate, when DCB was removed.

**Figure 3.** SEM images of the PTMA/SWNT (2 wt%) composite electrode. Scale bar: (a) 1 μm, (b) 400 nm.

### 5.3 Electrical Conductivity through Conductive Network

The PTMA/SWNT layer was fabricated by dropcasting on a glass or an ITO substrate and drying at 50°C. The composite was formed without surfacing or settling during the layer formation (the cross-sectional SEM image is shown in Fig. 3). The electrical conductivity of the PTMA/SWNT composite on a glass substrate in dry state was measured using the four-probe method. Fig. 4a shows the electrical conductivity of the composites prepared on a glass substrate. A power law relation was used to determine the threshold of electrical conductivity (eq. 1): \( \sigma_{RT} \propto (x - x_c)^\beta \), where \( \sigma_{RT} \), \( x \), \( x_c \), and \( \beta \) are the electrical conductivity, the loadings fraction of SWNTs, the percolation threshold, and the critical exponent, respectively.\(^{24,25}\) The fitting line (Fig. 2a inset) provided the low percolation threshold \( (x_c = 0.83, \beta = 3.2) \), which was comparable to the SWNT composite prepared via wrapping with poly(methylmethacrylate)\(^{26}\) and could be attributed to the high dispersion degree of the
SWNTs. No particular contribution of the pendant TEMPO group to the electrical conductivity under the dried or solvent-free condition could be seen. When vapor-grown carbon fiber (VGCF) was employed instead of SWNTs, the percolation threshold was not observed even after the addition of 10 wt% loading of VGCF (Fig. 7).

The charge propagation process in the layer of the PTMA/SWNT composite was analyzed with the Cottrell plots (Fig. 4a), assuming a semi-infinite diffusion at the early stage of the electrolysis (eq.2): 

\[ i_t = nFAC(D/\pi t)^{1/2} \]

where \( i_t, A, C, \) and \( D \) are a current, the geometrical surface of the ITO electrode, the concentration of the pendant TEMPO group, and the diffusion constant for the charge propagation, respectively. The slope obtained for the PTMA/SWNT composite was much larger than that of pristine PTMA (yielding an apparent diffusion constant \( D_{\text{app}} = 6.4 \times 10^{-10} \) and diffusion constant \( D = 1.2 \times 10^{-11} \text{ cm}^2 \text{s}^{-1} \) for the composite and PTMA, respectively), suggesting that the apparent charge diffusion was enhanced as a result of the increment of the effective interface area of the conductive SWNT network. It is worth to note that the electrode reaction requires electro-neutralization with counter-ions. While the counter-ion could diffuse rapidly in the composite exposed to the electrolyte, the relatively small swelling degree of the composite would maintain the percolation network of the SWNTs with \( \mu \text{m-scale film thickness.} \)

![Figure 4](image)

**Figure 4.** (a) Electrical conductivity of the PTMA/SWNT composite (solid line: the best fit line corresponding to eq. 1). Inset: conductivity as a function of the loading fraction of SWNT in a logarithmic scale. (b) Cottrell curves for chronoamperometry after applying a potential pulse from 0 to 1.0 V vs. Ag/AgCl. The PTMA/SWNT (thick solid curve) and PTMA (thick dashed curve) corresponding to a semi-infinite diffusion process in acetonitrile containing 0.1 M TBAClO\(_4\). Inset: Cyclic voltammograms of the PTMA/SWNT composite electrode (870 nm) at 0.5 mV s\(^{-1}\). 

### 5.4 Charge-Storage Performance of the Nanocomposite

A half-cell was fabricated, employing the PTMA/SWNT (4 wt%) composite electrode prepared on an ITO plate, a Pt wire, and Ag/AgCl as the working, counter, and reference electrodes, respectively. The amount of SWNTs was chosen from the end of percolation threshold in Fig. 4a where the sharp increment of conductivity turned into constant at high
conductivity (> 5.1 × 10^-1 S cm^-1). All electrodes were dipped into the acetonitrile electrolyte. The cyclic voltammogram of the composite gave a reversible redox wave at 0.78 V with a symmetric and narrow peak-to-peak separation (ΔE = 58 mV) (Fig. 4b, inset), indicating that redox reactions between the pendant TEMPO groups were stable without undesired reactions even in the thick layer of the composite electrode.

Figure 5. Discharging curves of (a) the PTMA/SWNT (4 wt%) composite, and (b) PTMA at the current density of 1, 3, 10, 30, and 60 A g^-1. Inset: Charging-discharging curves of the PTMA/SWNT composite at 1 A g^-1 in acetonitrile containing 0.1 M TBAClO_4. (c) Discharging capacity of the PTMA/SWNT (4 wt%) composite (black circle) and PTMA (white circle) with the thickness of 870 nm.

The charging and discharging curve of the PTMA/SWNT composite electrode exhibited a plateau voltage at 0.8 V (Fig. 3b inset), which is in agreement with the redox potential of the pendant TEMPO group of the PTMA (Fig. 4b inset). The charging and discharging capacity was almost same providing the Coulombic efficiency or the ratio of charging capacity vs. discharging capacity was found to be 93%. The rate performance at the high current density of 1–60 A g^-1 of the composite electrode is given in Fig 5c. The composite showed value of 91% (100 mAh g^-1) of the theoretical capacity (111 mAh g^-1) at 1 A g^-1 indicating that almost all pendant TEMPO groups in the composite actively contributed to the reversible charge-storage. On the other hand, the pristine PTMA showed only 21% (23 mAh g^-1) (Fig. 5a, b). While the discharging capacity of the pristine PTMA to 30 A g^-1 was tremendously decreased to 2% (2 mAh g^-1), the composite retained a capacity of 70% of the theoretical (75 mAh g^-1) even at 60 A g^-1, indicating a full discharging within 6 s. In general TEMPO-substituted polymers could exhibit a quantitative redox capacity with the thin film (<200 nm). Therefore, the polymer required the additive conductive carbon fiber for up-sizing to the micrometer scale thickness, which result in the loss of optical transmittance (see Supporting Information Fig. 7). However, these results demonstrated that the PTMA/SWNT succeeded in quantitative and reversible charging-discharging with keeping the transparency (Fig. 5a, Fig. 6a) at extremely high-rate.

Then optical transmittance of the PTMA/SWNT (4 wt%) composite on a glass substrate is demonstrated in Fig. 6a. In the visible region, PTMA showed the absorption maximum
\( \lambda_{\text{max}} (\varepsilon) = 458 \text{ nm} \left( 13 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \right) \), per pendant TEMPO group. The composite with 100 nm film thickness was almost colorless and kept a transmittance of >90% at 550 nm. The transparency decreased with an increment of the film thickness, but was retained 86%, even at with 580 nm of thick film thickness. The optical transmittance of the composite was found to be maintained after 500 charging-discharging cycles (Fig. 6b).

**Figure 6.** (a) Transmittance spectra for PTMA (dotted curve), and glass (thin solid curve), PTMA/SWNT (4 wt%) composite with 100 nm (dashed curve), and 580 nm film thickness (thick solid curve). Inset: a photograph of the PTMA/SWNT composite (1200 nm) on a glass substrate. (b) Transmittance at 550 nm after charging (white circle) and discharging (black circle) 500 cycles.

**Figure 7.** Photographs of PTMA/VGCF composite electrode. The loading fraction of VGCF of (a) 5, (b) 10, (c) 50, and (d) 90, and (e) 100 wt%.

In conclusion, novel composites of the radical polymer PTMA and SWNTs were prepared via the polymer-wrapping process using a combination of ultrasonication and ultracentrifugation without any surfactants. The TEM image analysis supports the efficient wrapping on a molecular level with a single-chain conformation of the PTMA polymer. The network of individualized SWNTs enhanced the charge propagation in the PTMA, thus providing a quantitative charge-storage capacity at a high rate. As far as we know, the amount of conductive materials is the smallest to form conductive pathway allowing the quantitative formula-based redox capacity. This fact suggested that this method is not only advantageous to a cathode-active material of so called “radical battery” but also to other potential application such as other rechargeable devices, counter electrodes for electrochromic devices, and other wet-type devices.
5.5 Experimental Section

Experimental

Materials

Purified SWNTs were purchased from BuckyUSA. The PTMA was synthesized as previously reported ($M_n = 4.1 \times 10^3$, $M_w/M_n = 2.0$, and unpaired electron content of 0.92 per the pendant TEMPO group). Tetrabutylammonium perchlorate (TBAClO$_4$) was obtained from Tokyo Kasei Co. All other reagents were obtained from Kanto Chemical Co. or Tokyo Kasei Co. and were used without further purification.

Preparation of the nanocomposite

Commercial SWNTs (1 mg) were ultrasonicated in o-dichlorobenzene (DCB) (2 mL) for 45 min at 0°C by a probe type sonicator (BRANSON 250AA), and the dispersion was centrifuged for 30 min at 1.6 $\times$ 10$^4$ g using a SIGMA 4-16K. The supernatant (500 $\mu$L) was added to the oxygen-free DCB (3 ml) solution of PTMA (5 mg). The loading fraction of SWNT was determined from residue obtained by drying up the supernatant (5 ml) to be 0.4 mg mL$^{-1}$ of SWNTs in DCB. The mixture was further ultrasonicated for 10 s at 0°C to exfoliate the aggregation homogeneously. The obtained dispersion of PTMA/SWNT was dropcast and dried using a vacuum oven at 60 °C on a glass and ITO to obtain electrochemical properties and electrical conductivity, respectively.

Measurement

The conductivity was measured using a 4-probe method (K-705RS KYOWARIKEN). The layer thickness of the composite was obtained using a surface analyzer (Tencor P-16+). UV-vis spectroscopic measurement was recorded by V-670 (JASCO). SEM and TEM observations were carried out using a JSM-7500F and JEM-2100F, respectively. The sample for the TEM measurement was prepared by dropcasting the PTMA/SWNT dispersion to a carbon-film-coated copper grid. The solvent was quickly soaked away by a filter paper and dried. Electrochemical measurements were performed on an ALS 660D electrochemical analyzer to obtain the voltammograms.

TEM images of the PTMA/SWNT composite.

The dispersion of PTMA/SWNT was dropcast on a carbon-film-coated copper grid. Both the polymer and SWNTs was held on the carbon film. Fig. 2 shows that a number of dispersed SWNTs were covered with PTMA. PTMA-wrapped SWNT apart from PTMA matrix was shown in Fig. S1b. It is difficult to obtain a higher magnification of SWNTs on the carbon film because few nano-meter thickness of the carbon film prevented focusing on SWNTs.
SEM images of PTMA/SWNT composite.

The cross-sectional SEM images of PTMA/SWNT composite are shown in Fig. S2. The PTMA/SWNT layer (2.7 μm) settled on ITO electrode (200 nm). A magnified image of the electrode in Fig. 3b shows that white spots corresponding to cross-sectional edges of SWNTs were well scattered in the PTMA. The average distance between each spots was ca. 260 nm obtained from spots number per 4 μm². These highly dispersed SWNTs suggest that SWNT kept individualized during the drying of the composite film at 75 °C, although dispersed SWNTs in DCB tend to aggregate, when DCB was removed.

Photographs of the PTMA/SWNT composite electrodes.

The PTMA and vapor-grown carbon fiber (VGCF, purchased from Showa Denko) were mixed and then dispersed by a similar method to that previously reported with the slight modification of using DCB instead of NMP. The dispersion was dropcast on glass substrate. Fig. 7 shows the photographs of PTMA/SWNT composites. Although in the case of the PTMA/SWNT a low loading fraction of SWNTs provided conductive film (Fig. 6a), the PTMA/VGCF composite at low loading fraction of VGCF formed the film (Fig. 7a, b) with partially aggregated VGCF and without measurable conductivity even at a 10 wt% loading of VGCF. Moreover, when the film contained a high loading fraction of VGCF, it showed conductivity but was found to be opaque, powdery, and brittle (Fig. 7c, d, and e). In general cathode active material of radical battery was consisted of PTMA, VGCF, and polyvinylidenefluoride (PVDF) as a plasticizer because VGCF decreased the smoothness of the composites for practical application.

Electrical conductivity of PTMA/SWNT composite.

The electrical conductivity of the PTMA/VGCF composite with 5, 10, 50, 90, 100 wt% of VGCF was measured by the four-probe method. The composite with 5 and 10 wt% of VGCF showed no measurable conductivity. The large loading fraction of VGCF (50, 90, and 100 wt%) showed a measurable conductivity of 13.5, 2.8, and 5.8 S cm⁻¹, respectively. However, these electrodes were found to be opaque and brittle, as discussed before. It could be stated that a lower aspect ratio (<100) of VGCF compared to SWNTs made it difficult to form conductive network at a low loading fraction.

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Chapter 6

Electrochemical Property of Radical Polymer-Grafted Carbon Nanotubes

6.1 Introduction

Modification of carbon nanotubes (CNTs) with functional polymers offers a promising method to provide a new functional π-conjugated material.\textsuperscript{1,2} CNTs impart a high electrical conductivity and a large surface area to the polymer. The coverage of the polymer around CNTs prevents nanotube bundling to impart dispersibility and functionality. The polymer-modified CNTs have been applied to preparation of various electrodes such as fuel cell catalysts and sensors.\textsuperscript{3-5} To propagate electrons over the electrode, a well-developed conductive pathway of CNTs is indispensable. However, polymer-modification often causes insulation by interfering interconnection between CNTs. A modification maintaining the connecting pathway could be a key point of modification.

Rechargeable batteries are of great interest on demand of present energy concerns. We have been developing “organic-based” rechargeable batteries using redox polymers as an electrode-active material.\textsuperscript{6-10} For cathode-active material, the radical polymers bearing densely populated robust radical pendant groups such as 2,2,6,6-tetramethyl-piperidin-yloxy (TEMPO) radical were synthesized by highly radical group-tolerant polymerizations such as a ring-opening metathesis polymerization\textsuperscript{11,12} and an anionic polymerization.\textsuperscript{13,14} Localized redox center at the radical pendant group allowed a high degree of doping per formula weight which led to a high charging-discharging capacity and determined the redox potential of the radical polymer. The cathode typically consisted of a radical polymer and a carbon nanofiber as a cathode-active material and a conductive additive, respectively.\textsuperscript{15-18} Optimum composition of the polymer and the conductive additive was empirically acquired on various conductive carbons, such as a vapor-grown carbon fiber and Ketjen black.\textsuperscript{16-18}

We have focused on CNTs having both a high aspect ratio and a mechanical strength essential for formation of the conductive network. Radical polymer-wrapped CNTs were well-dispersed in the radical polymer matrix and showed a high electrical conductivity,
allowing a rapid charging-discharging property.\textsuperscript{19} Although a significant number of conducting and charge-storable $\pi$-conjugated material has investigated, they have been suffering from low stability.\textsuperscript{20} The fact prompted us to synthesize a new charge-storage and conductive material by modification of CNTs with radical polymer.

![Scheme 1](image)

**Scheme 1.** (a) Schematic illustration and (b) chemical structure of the radical polymer-grafted MWNTs 1.

Polymer-grafting provides the strongest interaction between polymer and CNTs. Various polymers have been previously introduced via “grafting from” method such as a surface-initiated polymerization,\textsuperscript{21-24} where living radical polymerization was often utilized as the grafting.\textsuperscript{21,22} However, the grafted polymers are likely to cover up the CNTs unevenly, spoiling the excellent conductivity of CNTs and obscuring the polymer grafting density. Therefore, while the effect of polymer grafting on solubility has been reported, few has discussed the conductivity of the grafted polymer.\textsuperscript{23} In addition, it requires troublesome multi-step synthesis for the macroinitiator.\textsuperscript{22}

One simple approach for the radical polymer-grafted CNTs would be “grafting to” method using an end-modificated polymer.\textsuperscript{25} An end-modification called “vinyl type terminating”\textsuperscript{25,26} has been developed for ring-opening polymerization recently, which proceeded quantitatively under mild conditions. We utilized in this paper, the facile one-pot end-modification for the grafting of CNTs. The end-modified poly(2,3-bis(2’,2’,6’,6’-tetramethylpiperidinyl-N-oxyl-4’-oxy-carbonyl-5-norbornene) \textsuperscript{3} was grafted to MWNTs yielding the \textsuperscript{3}grafted MWNTs 1 (Scheme 1). TEM images revealed a core-shell structure of 1, which exhibited a unprecedented long-lasting and high rate charging-discharging property.

6.2 Preparation of Radical Polymer-Grafted to Multi-Walled Carbon Nanotubes

The end-modificated radical polymer \textsuperscript{3} was prepared by vinyl ester termination\textsuperscript{26} (Scheme 2) as follows. The TEMPO-substituted norbornene 2 was polymerized using Grubb’s 2nd generation catalyst as reported.\textsuperscript{11} Addition of a termination agent,
1-but-2-ene-1,4-diyl-4-bis(perfluorophenyl) dibutanedioate, into the polymerization mixture quenched the living polymer chain yielding the end-modified 3. MALDI-TOF mass spectrum of the end-modified 3 showed discrete mass peaks around 4800 g/mol by the equal interval of 491 g/mol corresponding to the molecular weight of the monomer unit in Fig. 1. The largest peak at 4333 g/mol was attributed to the 8-mer of the end-modified 3. The average degree of polymerization was 10 ($M_n = 5,800$, $M_w/M_n = 1.1$). The low polydispersity indicated both a fast initiation and end-modification of the polymerization. No other peak attributed to non-functionalized polymers was observed, indicating that the end-modification achieved a high yield. The spin concentration of the polymer per TEMPO pendant group was 96% determined from SQUID.
MWNTs (the diameter ca. 10 nm) were acid-treated to yield carboxylated MWNTs 4 (For detail preparation See Supporting Information). The product 4 was condensed with alkyl diamine to yield amino group-functionalized MWNTs 5. The weight-loss of 5 at 550°C was determined to be 27 wt% from TGA analysis (Fig. 2), which offered a basis to determine the 3-grafting density (vide infra). Then, 5 were condensed with the end-modified 3 in o-dichlorobenzene (DCB). The reaction mixture was sonicated and washed several times with chloroform to remove the ungrafted polymer. The filtrate was dried to yield the 3-grafted MWNTs 1. The grafting density was determined to be 0.28 chains/nm$^2$, or one chain per 140 carbons on the surface, from the 50 wt% weight loss of 1 at 550 °C (Fig. 2). The grafting density was similar to the report on “grafting to” functionalization of CNTs with well-defined polystyrene by “Huisgen cycloaddition”.24

### 6.3 TEM measurement of the Radical Polymer-Grafted MWNTs

TEM samples were prepared by drop-casting the dispersion of 1 in DCB on holey grid. A magnified image of 1 (Fig. 3a) shows a core-shell nanostructure with a polymer-thickness of 10±7 nm around the MWNT, which was consistent with the extended chain length of grafted 10-mer of 3. Fig. 3b shows an overview of 1. The 3-grafted MWNTs 1 were individualized well and yet aggregated closely. The polymer was attached around MWNTs.

The electrical conductivities were measured by 4-probe method. The conductivity of the pristine MWNTs, the amino group-functionalized MWNTs 5, and 1 were determined to be 4×10$^{-1}$, 7×10$^{-1}$, and 3×10$^{-4}$ S/cm, respectively. The conductivity of the amino group-functionalized MWNTs 5 was slightly lower than the pristine MWNTs (> 10$^{-1}$ S/cm). The mechanical mixture of 5 and the corresponding amount of 3 to the grafted 3 (7:3 in w/w) showed no measurable conductivity. It was likely that 3 placed between the MWNTs
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prevented intersite electron transfer, which would be critical to the bulk conductivity. It is worth to note that the polymer-grafted MWNTs 1 showed a relatively higher conductivity (> $10^{-4}$ S/cm) compared to the mixture of 5 and 3 though the conductivity of 1 was much lower than that of 5 by three orders of magnitude. The electrical conductivity of 1 was much higher than a redox polymer-grafted MWNTs obtained by “grafting from” method, suggesting that the distance between the tubes of 1 was sufficiently close for electrical conduction.

**Figure 3.** TEM images of 1. Scale bar: (a) 20 nm and (b) 100 nm.

6.5 Electrical Conductivity and Charge-Storage Performance of the Radical Polymer Grafted MWNTs

The dispersion of 1 was dropcast on an ITO electrode to form a layer. For comparison, a composite electrode consisted of 3 and MWNTs (3:7 in w/w) was also prepared. The cyclic voltammogram of the layer of 1 is shown in Fig. 3a. The layer of 1 showed reversible redox wave at 0.81 V attributed to TEMPO. The narrower adsorbate peak separation $\Delta E (= E_{pa} - E_{pc})$ of 1 (20 mV) compared to that of the composite electrode (52 mV) indicated an efficient electron-transfer of 1. It could be stated that the uniform grafting and close attachment of the radical polymer allowed homogeneous counterion accommodation and efficient electron-transfer between the 3 and MWNTs.

The redox capacities were determined from the time-integration of the redox waves. The composite layer exhibited 39 mAh/g of capacity per 3. The capacity loss could be caused by large aggregates of 3. In contrast, the 3-grafted MWNTs 1 exhibited 90 mAh/g per the grafted 3 corresponding to the theoretical capacity of 3 (109 mAh/g), or 28 mAh/g per the 3-grafted MWNTs 1. This exhaustive redox capacity indicated that uniformly grafted 3 allowed efficient electron-exchange between the radical pendant groups by homogeneous counterion accommodation and high conductivity. It may be noted that the layer of 1
exhibited a high redox capacity even with the layer thickness of 800 nm, which was much thicker than maximum thickness (<300 nm) of the pristine polymer layer that could exhibit a quantitative capacity with respect to the theoretical capacity. The cycle performance of the discharging capacity of 1 and the composite were shown in Fig. 4b. The discharging capacity of 1 showed 91% of the first cycle after 2000 cycles while that of the composite was decreased to 74% after 1000 cycles. The 3-grafted MWNTs 1 demonstrated the highest charging/discharging stability among the reported redox-active molecules.

Figure 4. (a) Cyclic voltammetry of 1 (solid curve), and the corresponding composite of 3 and MWNTs (broken curve) in acetonitrile containing 0.1 M TBAClO₄. (b) Cycle performances of 1 (●) and the composite electrode (○). Scan rate = 1 mV/s. The rate dependent discharging performance (c) of 1 and (d) of the composite layer. The layer thickness was 800 nm.

The rate performance of 1 and the composite was shown in Fig. 4 at 60—600 C. The discharging curve of 1 at 60 C-rate showed a plateau voltage at 0.8 V vs. Ag/AgCl and the discharging capacity of 90 mAh/g. The discharging capacity was maintained even at 600 C (corresponding to the full discharging for 6s), while the composite showed a large potential drop due to the low electrical conductivity.

In conclusion, we synthesized a new π-conjugated material based on CNTs with both charge-storage property and electron conductivity. The “grafting to” approach allowed the uniform coverage of the functional polymer around MWNTs to form a core-shell structure with a high radical polymer grafting density of 0.28 chains/nm², which offered high dispersibility allowing wet-type processing. The high swellability and robustness of the radical polymer grafted MWNTs were demonstrated by the high redox capacity and the
fadeless cycle performance. The new material and design would be valuable not only for a charge-storage material but also for a building block for potential wet-type applications.\textsuperscript{28,29}

### 6.5 Experimental Section

**Materials and Methods**

All Chemicals were purchased from TCI, Aldrich and Kanto Chem. Co. Multi-walled carbon nanotubes were purchased from Hanhwa Nanotech and used without further purification. \textsuperscript{2,3} 2,3-bis(2',2',6',6'-tetramethylpiperidinyl-N-oxyl-4'-oxy-carbonyl-5-norbornene \textsuperscript{2} and 1-but-2-ene-1,4-diy-4-bis(perfluorophenyl) dibutanedioate was prepared as reported.\textsuperscript{11,26}

**Measurements**

Electrochemical measurements were performed using an electrochemical analyzer model 660D (ALS). All measurements were performed under an atmosphere of dry argon. The formula weight-based theoretical capacity (in mAh g\textsuperscript{-1}) was calculated according to 1000 \( nFM \)\textsuperscript{1} (3600)\textsuperscript{-1}, where \( n, F \) and \( M \) are stoichiometric number of electrons, the Faraday constant and the molar mass of the repeating unit, respectively. The redox capacity (in mAh/g) was obtained employing 1000 \( Qm \)\textsuperscript{1} (3600)\textsuperscript{-1}, where \( Q \) and \( m \) are charge passed in electrolysis and the loading weight of the polymer. The 1 C-rate is defined as the current density at which the charging or discharging of the cell takes 1h. A one-component cell with a glassy carbon plate electrode, a platinum wire and a Ag/AgCl electrode as the working, the counter and the reference electrodes, respectively, were employed to obtain the voltammograms. X-ray photoemission spectroscopy (XPS) elemental analysis was performed by JPS-9010TR (JEOL). TGA analyses were performed by TG/DTA 220 (Seiko Instruments Inc.) under an atmosphere of nitrogen.
References

Chapter 7

Future Prospects

7.1 Conclusion

In this thesis, the author described the preparation of novel electron-acceptor type polymers such as poly(2-vinyl anthraquinone) and polyaromatic imide. They demonstrated their own performance based on the molecular structures as high-density charge-storage devices. In this chapter, the characteristics of these polymer and a number of important conclusions emerging from this study are summarized.

In chapter 2, anthraquinone was grafted to polystyrene backbone to yield polyanthraquinone with high anthraquinone-loading amount, which contained quantitative amount of anthraquinone according to the $^1$H-NMR analysis. The method is characterized by the high efficiency compared to previous report using Friedel-Crafts reaction (<49%). The drastic dissolution of reduced anthraquinone in contrast to low solubility of the neutral hampered the utilization of anthraquinone redox to electrochemical purpose. The backbone allowed cyclable stability in organic electrolyte during electrochemical reduction and oxidation, combined with conductive carbon. It is provably attributed to the entanglement of the aromatic pendant groups. Interestingly, the polyanthraquinone were swellable even in the aqueous electrolyte, providing clear insight of aqueous electrochemistry that the constantaneous 2-electron redox peak appeared in aqueous electrolyte. This result prompted us to investigate how aqueous electrolyte stabilizes the electron-transfer reaction of anthraquinone. As Smith et al. suggested that hydrogen-bonding mainly stabilized redox

Electrochemistry of anthraquinone was more eagerly explored in organic electrolyte than aqueous electrolyte due to insolubility of anthraquinone. Therefore, almost all researchers have reported electrochemical behaviors of anthraquinone in organic electrolyte. There are considerable amount of surveys with respect to stabilization of reduced anthraquinone by hydrogen bonding. Generally, proton donor molecules such as alcohols formed single/multi-point hydrogen bonding to hydrogen-acceptor of quinone. The
formation of the hydrogen bonding was dependent on the concentration of reactants and the number of charges in reduced anion where more negative anions tend to associate with more hydrogen-donors. That causes difference between that in organic electrolyte and practical conditions in aqueous electrolyte, hindering appropriate comparison between the two. We assumed that anthraquinone form hydrogen-bonding in aqueous electrolyte even at neutral (not reduced) state because anthraquinone was surrounded by H₂O molecules. To simulate the condition, the anthraquinone self-forming hydrogen-bonding was selected as model molecules that could be investigated by electrochemical analysis in organic solvent. Anthraquinone derivatives with forming intra-molecular hydrogen bonding(s) are synthesized by condensation. The anthraquinones showed thermodynamically stabilized electrochemical behavior corresponding to the number of hydrogen-bondings. The electron transfer rate of anthraquinones was also enhanced with stabilization. The result suggested clear advantage for the use of polyanthraquinone bearing multi-point hydrogen-bonding, which could allow rapid self-electron exchange reaction between pendant redox centers.

In chapter 3, poly(2-vinylanthaquinone) (PVAQ) was designed and synthesized. Though low solubility of the corresponding monomer made it difficult to achieve polymerization without precipitation, 1,2-dichloroethane solubilized both the monomer and the polymer to provide high molecular weight. The obtained PVAQ was applied as a new class of anode-active material for rechargeable polymer/air battery where atmospheric oxygen was employed as a cathode-active material. Even though PVAQ showed few redox capacities without swelling in pH 7, the capacity was drastically increased over pH 12 corresponding to the dissociation of proton. The operation as negative charge-storage materials in strongly basic conditions enabled the utilization of oxygen-reduction cathode. It is worth to note that PVAQ could demonstrate stable charge-discharge performance over 300 cycles in the open system polymer/air battery cell. The charge-storage was strikingly robust and largest among n-type redox materials such as π-conjugated and non-conjugated polymers.

In chapter 4, capability of polyaromaticimides (PAI) as charge-storage device was demonstrated. There are few reports on PAI though aromatic small molecules containing imide moieties showed excellent electron-transporting properties in organic thin film transistor. The same was observed in the mixture of PAI grinded with conductive carbons. However, when the polyamicacid of the PAI precursor was combined with carbons in solution state and then thermally imidized, the obtained PAI-electrodes provided n-type charge-storage property attributed to the reduction of PAI at negative potential (<-1.0 V) and persisted for more than 100 cycles. The preparation method could offer efficient swelling to polyimides which is key for n-type redox activity.

In chapter 5, single-walled carbon nanotubes (SWNTs) were dispersed and wrapped with a radical polymer, 2,2',6,6'-tetramethylpiperidine-oxy-methacrylate (PTMA). The
PTMA-wrapped SWNTs were highly stable and homogeneous in organic solvent, drop-casted to thin layer electrode. The formation of conductive pathway at low loading amount of SWNTs in PTMA allowed the electrode transparent. The electrode extracted exhaustive formula-weight based capacity of PTMA with extremely small amount of SWNTs.

In chapter 6, a molecular weight-defined and end-modified radical polymer of redox-active nitroxide radical was uniformly grafted to multi-walled carbon nanotubes with high conductivity, which exhibited a high rate and fadeless charge-storage capability. The radical polymer was uniformly grafted to MWNTs.

7.2 Future Prospect

In this thesis, fairly stable n-type redox active polymers were synthesized and demonstrated charge-storage properties. Anthraquinone accepted 2 electrons to form dianion without self-decomposition, and protonation. In addition, the reduced state was sufficiently stable in the open system cell exposed to the air containing O2. The results are interesting because generally reduced state of organic material is unstable. As discussed in Chapter 1, i.e. heterocyclic compounds containing nitrogen atom was fragile. Carboanion is highly reactive to proton. Although ammonium cation shows more positive redox potential than reduction potential of H2O, the reduced amine is reactive to O2. The fact made the utilization of polyviologen as charge-storage material difficult. Though a negative potential was required for anode-active material to exhibit a large potential gap from a cathode active material, a more negative potential than the reduction potential of O2 (< 0.5 V) leads to react with O2. To break out the dilemma a strategy of “O2 barrier” by forming closely packed structure was widely used for stable n-type molecules in TFT devices. Some excellent examples such as naphthalenediimide (NDI) bearing fluorinated alkyl chains showed highly

![Figure 1. Two-electron reduction of anthraquinone in aqueous electrolyte](image-url)
stable n-type TFT operations. However, redox polymers have to swell for accommodation of counterions which contradict to form O₂ barrier based on close packing. There were few investigations and clear strategy for stable electron-acceptor type polymer.

The stable behavior of poly(2-vinylanthraquinone) (PVAQ) gave us general insights for stable organic anion. At first, hydrogen-bonding is not same as protonation which form a covalent bond with oxygen atom but stabilize the anions similarly to electrostatic interaction. When the protonation was prevented in a basic condition, hydrogen-bonding could form stabilizing the anion even in the water (Figure 1).

Secondly, hydrogen-bonding could form at multi-point surrounding the anion and electrostatically stabilize the anion to achieve 2 e⁻ reductions at a redox potential. Usually the second electron transfer proceeds at more negative potential that the first. It caused decomposition of electrolyte.

Finally, it would appear that the surrounding hydrogen-bonding not only electrostatically stabilized but sterically hindered the anion. This behavior was observed in the anion radical of growing end in the anionic polymerization of methacrylate, where cation reduced the reactivity of anion and governed the tacticity of PMMA. The assumption could offer a comprehensive explanation to the fact that the reduced anthraquinone was fairly stable in aqueous electrolyte though reduced viologen was highly reactive to O₂. It might be caused by hydrophobicity of the reduced viologen which could be exposed without solvation. The basket of the hydrogen-bondings acted like bulky alkyl groups that were employed in robust organic radicals to prevent undesired radical reactions such as dimerization of unpaired electrons.

**Figure 2.** Negative-charge mediation with n-type redox polymer modified electrode for reduction

The unprecedented stable polyanion could be attractive for CO₂ reduction electrode which is essential process in artificial photosynthetic system (Figure 2).¹ PVAQ showed highly negative redox potential almost at the limit of H₂O decomposition. Given that the reduction electrodes suffer from low efficiency due to preferential H₂ production regarding
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CO$_2$ reduction in aqueous solutions. The reduced PVAQ at negative potential is expected to work as a heterogeneous reducing agent for CO$_2$ with avoiding H$_2$ generation. For more stable n-type redox behavior of PVAQ, the more stable n-type doped state is necessary.

![Figure 3](image)

**Figure 3.** (a) p- and (b) n-type doped single-walled carbon nanotubes.

Lee and Choi et al. reported that pristine semiconducting SWNTs showed p-type semiconducting behavior. n-Type dope of SWNT by reduced viologen could change the polarity of TFT operation. The carrier tunability is attractive especially in the case of n-type doping. The n-type doped state could be more achievable by using redox polymer that highly containing redox centers.

![Figure 4](image)

**Figure 4.** Bulk hetero junction solar cell using the conductive network of CNTs.

It is also attractive to utilize conductive network of carbon nanotubes in redox polymers. Bulkhetero junction cell is of interesting for a number of researchers, which consisted generally of p-type p-conjugated polymer and n-type molecules such as polythiophene and fullerene, respectively. The interface between the two components plays an important role in the charge separation. Large interface and continuous phase are essential factors for efficient charge-separation. However, those required troublesome crystallization process or phase separation process. The conductive network of carbon nanotubes could offer both large surface area and highly conductive pathway by facile process due to the high aspect ratio and mechanical strength. The conductive network is expected to be useful not only for charge-storage devices but also for a new type of p/n jointed device such as photo-voltaic cells.
References


List of Publications

   “Radical Polymer-Wrapped SWNTs at a Molecular Level: High-Rate Redox Mediation through Percolation Network for a Transparent Charge-Storage Material”

2. **Wonsung Choi**, Daisuke Harada, Kenichi Oyaizu, Hiroyuki Nishide
   “Aqueous Electrochemistry of Poly(vinylanthaquinone) for Anode-Active Materials in High-Density and Rechargeable Polymer/Air Batteries”

3. Kenichi Oyaizu, **Wonsung Choi**, Hiroyuki Nishide
   “Functionalization of Poly(4-chloromethylstyrene) with Anthraquinone Pendants for Organic Anode-Active Materials”

4. Kenichi Oyaizu, Akihiko Hatemata, **Wonsung Choi**, Hiroyuki Nishide
   “Redox-active Polyimide/Carbon Nanocomposite Electrodes for Reversible Charge Storage at Negative Potentials: Expanding the Functional Horizon of Polyimides”

5. **Wonsung Choi**, Kenichi Oyaizu, Hiroyuki Nishide
   “Enhanced Electron-Transfer Reaction of Intramolecular Hydrogen Bonding-Functionalized Anthraquinones for Rapid Charge-Storage”

6. **Wonsung Choi**, Shogo Endo, Kenichi Oyaizu, Hiroyuki Nishide, Kurt E. Geckeler
   “Uniform Grafting of TEMPO-Radical Polymer around Multi-Walled Carbon Nanotubes: A Robust and Efficient Charge-Storage Material”
   *Chemical Communications*, submitted.

List of Awards


2. The best Poster Award of 3rd WCU symposium on Nanobio Materials and Electronics (2009)
List of Presentations

1. “Functionalization of Single-Walled Carbon Nanotube Wrapped with Radical Polymer for a Transparent Charge-Storage Material”
   *2011 MRS Fall Meeting & Exhibit*, Boston, USA, December 2011.
   Wonsung Choi, Kenichi Oyaizu, Hiroyuki Nishide, Kurt. E. Geckeler

   *International Conference on Nanomaterials and Nanotechnology NANO-2010*, Tamil Nadu, India, December 2010.
   Wonsung Choi, Seok-Ju Choi, Hiroyuki Nishide, Kurt. E. Geckeler

3. “Nanocomposite of Single-Walled Carbon Nanotubes and Poly(TEMPO-substituted Methacrylate) toward a Transparent Charge-Storage Devices”
   Wonsung Choi, Kenichi Oyaizu, Hiroyuki Nishide, Kurt. E. Geckeler

4. “Radical Polymer/SWNT Nanocomposite toward a Transparent Charge-Storable Material”
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   Wonsung Choi, Seok-Ju Choi, Kenichi Oyaizu, Hiroyuki Nishide, Kurt. E. Geckeler

5. “Synthesis of Aliphatic Polyatnthraquinone and Application as an Anode-Active Material”
   Wonsung Choi, Daisuke Harada, Kenichi Oyaizu, Hiroyuki Nishide

6. “Electrochemical Property of Anthraquinone-Substituted Polymethacrylamide”
   Wonsung Choi, Daisuke Harada, Kenichi Oyaizu, Hiroyuki Nishide

7. “Polyantraquinone Electrode for n-type Anode-Active Material”
   Wonsung Choi, Kenichi Oyaizu, Hiroyuki Nishide

8. “Anthraquinone-Substituted Non-Conjugated Polymers for Anode-active Materials in Organic Secondary Batteries”
   Wonsung Choi, Kenichi Oyaizu, Hiroyuki Nishide

9. “Anthraquinone-Functionalized Redox Polymers for Charge-Storage Application”
   Wonsung Choi, Kenichi Oyaizu, Hiroyuki Nishide

10. “Synthesis and Redox Property of Nitroxide Radical-Substituted Triphenylamine and redox property”
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List of Patents

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2. “Quinone-Polymer Electrode, Charge-Storage Material, and Battery”  
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4. “Radical Polymer Wrapped Carbon Nanotube for Charge-Storage Material”  
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