— Article —

Surface Modification of Carbon Fiber by using Electro-oxidation and -reduction Sequential Procedure

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A new method for the surface modification of carbon fiber by using electro-oxidation and -reduction sequential procedure has been exploited. The introduction of hydroxyl groups on carbon fiber was attained by the electrooxidation of the NO_3 anion containing electrolyte using the carbon fiber as an anode, and the anodically introduced hydroxyl groups were successively transferred to the alkoxy groups by the electroreduction in the presence of alkyl halides using the oxidized carbon fiber as a cathode. The functional groups introduced on the carbon fiber were estimated by the X-ray photoelectron spectroscopy, the observation of the hydrophilicity of the carbon fibers, and also by using the carbon fibers as cathodes for the electroreduction of acetophenone (**1**). The diastereoselectivity of the reduced product, 2,3-diphenyl-2,3-butanediol (**2**), in the electroreduction of **1** indicated the interaction between the electrogenerated radical anion species of **1** with the hydroxyl groups on the carbon fiber surface, and the *dl/meso* ratio was found to increase with an increase in the content of the hydroxyl groups on the carbon fibers. The sequential modification method for carbon fibers in one-pot was successfully performed by using the $\text{MeCN-H}_2\text{O}$ (3 : 1) mixed solvent containing the mixed supporting electrolytes $\text{Bu}_4\text{NNO}_3\text{-Bu}_4\text{NClO}_4$ (1 : 1) and alternating the polarity of the electrodes to give the carbon fibers having high content of hydroxyl or alkoxy groups.

Key Words : Carbon Fiber, Surface Modification , Sequential Treatment, Acetophenone

1 Introduction

The surface modification of carbon fibers provided not only new surface structure which influences their physical property but also new function in the use for the electrochemical reaction as electrodes.^{1, 2)} The modification of carbon fibers has been well studied and several practical methods have been already established.^{3 - 17)} The surface oxidation of the carbon fiber are usually required^{3 - 12)} since the carbon fiber surface is originally hydrophobic and less reactive to the reagents for the introduction of the functional molecules on the carbon fiber. We have already achieved the introduction of hydroxyl groups on the carbon fiber surface using NO_3 radicals generated by the electrooxidation of NO_3 anions.¹⁸⁾ More recently we have also reported the electroreductive modification method in which the anodically introduced hydroxyl groups on the carbon fiber react with the added electrophiles to form the ether bondings under the cathodic reaction conditions.¹⁹⁾ Several functional molecules such as β -cyclodextrin were successfully fixed on the carbon fiber, however, the content of the introduced functional molecules was not enough high to show remarkable effects of the functional molecules when the resulting carbon fibers were used as the modified electrodes. In our modification method the amount of the introduced functional molecules on the carbon fiber depends on the amount of hydroxyl groups introduced in the first anodic oxidation step. However the control of the anodic oxidation of the carbon fiber surface is not always easy and the over-oxidation often brings undesired effect on the resulting carbon fiber. It was reported

that excess treatment of carbon fibers under the conditions of plasma oxidation resulted in the further oxidation of the acidic functional groups that were introduced by the first oxidation of the carbon fiber surface.⁷⁾ The similar phenomenon was also observed in the electrochemical method.⁸⁾ In this study we have investigated the correlation between the supplied electricity and the content of the hydroxyl groups on the carbon fibers, and performed successively the electrooxidation and electroreductive modification of carbon fibers to afford the modified carbon fibers having high content of alkoxy groups without over-oxidation. The surface character of carbon fibers were evaluated by comparing their hydrophilicity and performance as cathodes in the electroreduction of acetophenone.^{20 - 23)} Moreover, the electrolyte was optimized for the sequential procedure of the electrooxidation and the electroreductive modification of carbon fibers in one-pot by alternating the polarity of the electrodes.

2 Experimental

2.1 Measurement

The constant electrocurrent was supplied with a Takasago GP-050-2 regulated DC power supply. X-ray photoelectron spectroscopy (XPS) measurements were acquired using a Shimadzu ESCA 3200 with a Mg X-ray source under vacuum of 10^{-5} - 10^{-7} mmHg. IR spectra were obtained on a Jasco FT-IR-470 Plus spectrometer. ^1H NMR spectra were measured on a Varian OXFORD NMR 300 (300 MHz). FT-NMR spectrometer and the chemical shift values (δ) were expressed in ppm down-

field from the internal TMS standard.

2. 2 Materials

Carbon fiber (felt type) was washed with acetone and dried *in vacuo* for 1 h just before use. Acetophenone was distilled *in vacuo* (59 °C/25 mmHg) under Ar atmosphere. Et₄NOTs was prepared from ethyl tosylate with triethylamine in ethanol and purified by the recrystallization from acetone. *N,N*-Dimethylformamide (DMF) was distilled to remove water as benzene azeotrope and purified by distillation (77 °C/50 mmHg) under Ar atmosphere. Lithium nitrate (LiNO₃), tetrabutylammonium perchlorate (Bu₄NClO₄), tetrabutylammonium nitrate (Bu₄NNO₃), acetonitrile (MeCN), distilled water (H₂O), 1-bromobutane, dimethylsulfoxide (DMSO), hexanoic anhydride, lithium aluminum hydride (LAH) and the other materials were commercially available and used without further purification.

2. 3. 1 Electrooxidation of the untreated carbon fiber

A solution of LiNO₃ (5 mmol) as a supporting electrolyte in the mixed solvent (MeCN : H₂O = 10 : 1, 55 mL) was put into an undivided electrolysis cell equipped with a carbon fiber anode (30 × 10 × 7 mm) and a Pt (20 × 20 mm) cathode. The electrooxidation was carried out under the conditions of constant current (200 mA) with cooling by an ice bath. After 3 F/mol of electricity based on the supporting electrolyte was passed, the carbon fiber anode was placed on a Soxlet type extractor and washed with running water for 1 h followed by acetone for 1 h, and then dried *in vacuo* for 1 h.

2. 3. 2 Electroreductive modification of the oxidized carbon fiber with 1-bromobutane

A solution of 1-bromobutane (5 mmol) as an electrophile and Bu₄NClO₄ (5 mmol) as a supporting electrolyte in DMF (30 mL) as solvent was put into an undivided electrolysis cell equipped with a carbon fiber cathode (30 × 10 × 7 mm) and a Pt (20 × 20 mm) anode. The electroreduction was carried out under the conditions of constant current (200 mA) with cooling by an ice bath. After 4 F/mol electricity based on 1-bromobutane was passed, the carbon fiber cathode was placed on a Soxlet type extractor and washed with running water for 1 h followed by acetone for 1 h, and then dried *in vacuo* for 1 h.

2. 3. 3 Electroreduction of acetophenone by using the electrochemically treated carbon fiber electrode

A solution of acetophenone (**1**) (10 mmol) in a mixed solvent (MeCN : H₂O = 3 : 1, 60 mL) in the presence of Et₄NOTs (5 mmol) as a supporting electrolyte was put into an undivided electrolysis cell equipped with the modified carbon fiber (30 × 10 × 7 mm) anode and Pt (20 × 20 mm) cathode. The electroreduction was carried out under the conditions of constant current (200 mA) with cooling by an ice bath. After 1 F/mol of electricity based on acetophenone was passed, the reaction mixture was extracted with diethylether (50 mL × 3) and washed with saturated NaCl aq and saturated NaHCO₃ aq. The combined organic layers were dried over anhydrous MgSO₄ and concentrated. The crude product was purified by a silica gel column chromatography (hexane : ethyl acetate = 10 : 1) to afford 2,3-diphenyl-2, 3-butanediol (**2**) as the coupling products and 1-phenylethanol (**3**).

The products (**2** and **3**) and *dl/meso* (2a / 2b) ratio of diol **2** were determined by ¹H NMR according to the methods outlined in Refs.^{24, 25)}

2,3-Diphenyl-2,3-butanediol (2) : IR (KBr) 3495, 1447, 1141, 1064, 764, 702 cm⁻¹; ¹H NMR (CDCl₃) δ 1.50 (s, 6H, *dl*-isomer), 1.60 (s, 6H, *meso*-isomer), 2.50 (br, 2H), 7.15-7.30 (m, 10H).

1-Phenylethanol (3) : IR (KBr) 3666, 3072, 3036, 2939, 2885, 1494, 1448, 1384, 1043, 740, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 1.50 (d, 3H, *J*=4.0 Hz), 4.84-4.96 (q, 1H, *J*=4.0 Hz), 7.25-7.40 (m, 5H).

2. 3. 4 Reduction of modified carbon fiber by using LAH

The modified carbon fiber (30 × 10 × 7 mm) was put into a solution of LAH (5 mmol) in THF (50 mL). After stirring for 24 h under Ar atmosphere at room temperature, the resulting carbon fiber was placed on a Soxlet type extractor and washed with running water for 1 h followed by acetone for 1 h, and then dried *in vacuo* for 1 h.

3 Results and Discussion

3. 1 Hydrophilicity of electrochemically oxidized carbon fibers

We have reported in the previous studies^{18, 19)} that the phenolic hydroxyl groups are introduced on carbon fiber by the electrooxidation of the LiNO₃ containing electrolyte using the carbon fiber as an anode. The amount of hydroxyl groups on the carbon fiber introduced under these anodic oxidation conditions depended on the supplied electricity, however, the increase of the electricity did not increase linearly the amount of the hydroxyl groups. The introduction extent of hydroxyl groups on the carbon fibers obtained under the conditions of several supplied electricities was evaluated by the observation of hydrophilicity (Scheme 1, Table 1). Because the felt type CF surface was too rough to measure its contact angle, the hydrophilicity of resulting CF was determined by the rapidness of the absorption of a drop of water.

The untreated carbon fiber (CF) showed hydrophobic character, and the carbon fiber was still hydrophobic after 100 C of supplied electricity was passed (entries 1, 2). On the other hand, after more than 200 C of electricity was passed, the resulting carbon fibers began to show the hydrophilicity, and the hydrophilicity was confirmed to increase with an increase of the supplied electricity (entries 3-7). The increase of the hydrophilicity corresponds to the contents of the hydroxyl groups introduced on the carbon fibers, and it is supported by the C 1s spectra that the peaks of the resulting carbon fibers attributed to the phenolic hydroxyl groups. The O/C

Scheme 1 Electrooxidation of untreated CF.

Table 1 Electrooxidation^{a)} of untreated carbon fiber.

Entry	Supplied electricity (C)	Hydrophilicity of resulting CF
1	0	Hydrophobic ^{c)}
2	100	Hydrophobic ^{c)}
3	200	Partially hydrophilic ^{d)}
4	500 (1 F/mol ^{b)})	Less-hydrophilic ^{c)}
5	720 (1.5 F/mol ^{b)})	Hydrophilic ^{d)}
6	1440 (3 F/mol ^{b)})	Hydrophilic ^{d)}
7	2160 (4.5 F/mol ^{b)})	Hydrophilic ^{d)}
8	2880 (6 F/mol ^{b)})	Less-hydrophilic ^{c)}

^{a)} The electrooxidation was carried out in a solution of LiNO₃ (5 mmol) in MeCN-H₂O (10 : 1) (55 mL). ^{b)} Approximately based on LiNO₃. ^{c)} Both faces of carbon fiber surface shed a drop of water. ^{d)} Both faces of carbon fiber surface absorbed a drop of water partially. ^{e)} Both faces of carbon fiber surface absorbed a drop of water. ^{f)} Both faces of carbon fiber surface absorbed a drop of water rapidly.

strength of CF- α . with 3 F/mol electricity (entry 6) was determined to be 43.3 % which was higher than that of the untreated CF (11.8%) or the chemically oxidized CF by K₂Cr₂O₇ in H₂SO₄ (26.8%). However, more than 2880 C of supplied electricity (6 F/mol based on LiNO₃) was found to give a less hydrophilic surface of the carbon fiber (entry 8). It is probably due to the over-oxidation, that is, the introduced hydroxyl groups seem to be further oxidized to other substituents and structures such as carboxylic acid and quinone structure. The surface study of the resulting carbon fibers by the XPS, in which the peaks of the carbonyl groups at 288.6 eV were observed, also supported this concept.

3. 2 Electroreduction of acetophenone by using the oxidized carbon fibers

The content of hydroxyl groups has been also evaluated by using anodically oxidized CFs as cathodes in the electroreduction of acetophenone (**1**) (Scheme 2, Table 2). Under the conditions using Et₄NOTs as a supporting electrolyte and the MeCN-H₂O mixed solvent, only diol **2** was obtained in *ca.* 50% conversion (50% of **1** was recovered) and 1-phenylethanol (**3**) was not produced. The *dl/meso* ratio of diol **2** in the electroreduction using 1 F/mol (based on LiNO₃) oxidized carbon fiber (CF- α) was increased to 4.3 from 3.0, the ratio observed in the electroreduction using the untreated CF (entries 1, 2). This diastereoselectivity was explainable by the mechanism shown in Fig. 1.^{18, 19)} The anion radical species generated by the electroreduction of acetophenone (**1**) are protonated in the protic media to form the radical species. The protonated radical species are then fixed on the CF surface by the interaction based on the hydrogen bonding between the alkoxides on the carbon fiber surface with the hydroxy groups of the radicals, and *dl*-isomer favorably forms because of the steric repulsion between the phenyl groups. In the electroreduction of **1** in MeCN-H₂O (10 : 1) as a less protic media there were not much difference in the diastereoselectivity of **2**. The *dl/meso* ratio of **2** using the untreated CF was 2.5 (yield 22%), while the *dl/meso* ratio of **2** using the untreated CF was 2.3 (yield 23%). The anion radical species are

Scheme 2 Electroreduction of acetophenone.**Table 2** Electroreduction^{a)} of acetophenone using oxidized carbon fiber electrodes.

Entry	Supplied electricity in electrooxidation ^{b)} (F/mol)	Conversion of 1 to 2 ^{c)} (%)	<i>dl/meso</i> (2a/2b) ^{c)}
1	0 (Untreated FC)	47	3.0
2	1	48	4.3
3	2	57	4.4
4	3	45	5.3
5	4	47	5.4
6	5	47	5.1

^{a)} The electroreduction was carried out in a solution of **1** (10 mmol) in MeCN-H₂O (3 : 1) (60 mL) in the presence of Et₄NOTs (5 mmol). The electricity was 1 F/mol based on **1**.

^{b)} Based on LiNO₃. ^{c)} Determined by ¹H NMR in CDCl₃.

Fig. 1 Plausible interaction between acetophenone ketyl radicals with the CF- α surface.

probably not protonated enough to interact with the alkoxides on the CFs in the less protic media. The *dl/meso* ratio of **2** increases with an increase of the supplied electricity in the electrooxidation of carbon fibers (entries 3-5), and the increase of the *dl/meso* ratio seems to correspond to the amount of the anodically introduced hydroxyl groups on the carbon fiber surface. Four F/mol (based on LiNO₃) of electricity for the electrooxidation of carbon fiber gave the oxidized carbon fiber that afforded highest *dl/meso* ratio of **2** in the electroreductive coupling of **1**, however the peak of carbonyl groups was confirmed at 288.6 eV in the spectrum of the carbon fiber by XPS. When the supplied electricity exceeded 5 F/mol based on LiNO₃, the *dl/meso* ratio of **2** decreased (entry 6). These results indicate that the undesirable over-oxi-

Scheme 3 Sequential surface modification of CF under the conditions of a) 3 F/mol electricity of electrooxidation in MeCN-H₂O (10 : 1) solution (55 mL) of LiNO₃ (5 mmol) and b) 4 F/mol electricity of electroreductive modification in the presence of 1-bromobutane (5 mmol) in DMF solution (50 mL) of Bu₄NClO₄ (5 mmol).

Table 3 Electroreduction^{a)} of acetophenone by using the sequentially treated carbon fiber

Entry	Cathode	Hydrophilicity of CF	Conversion of 1 to 2 ^{b)} (%)	<i>dl/meso</i> (2a/2b) ^{b)}
1	Untreated CF	Hydrophobic ^{c)}	47	3.0
2	CF-ox.	Hydrophilic ^{d)}	45	5.3
3	CF-mod. Bu	Hydrophobic ^{c)}	49	3.7
4	CF-mod-ox.	Hydrophilic ^{d)}	45	5.0
5	CF-mod-mod. Bu	Hydrophobic ^{c)}	48	4.2

^{a)} The electroreduction was carried out in a solution of **1** (10 mmol) in MeCN-H₂O (3 : 1) (30 mL) in the presence of Et₄NOTs (5 mmol). The electricity was 1 F/mol based on **1**. ^{b)} Determined by ¹H NMR in CDCl₃. ^{c)} Both faces of carbon fiber surface shed a drop of water. ^{d)} Both faces of carbon fiber surface absorbed a drop of water rapidly.

dation starts at *ca.* 4 F/mol of electricity, and the supplied electricity was fixed to 3 F/mol in the electrooxidation. This optimized supplied electricity shows good agreement with that determined by the observation of the hydrophilicity of the carbon fibers (Table 1 in the previous section).

3. 3 Electrochemical sequential modification of carbon fibers

The increase of the hydroxyl groups on the carbon fiber enhances the possibility of the over-oxidation, and the content of hydroxyl groups shows the maximum during the electrooxidation of carbon fibers. The over-oxidation seems to be inevitable in the single-step electrooxidation. Then we have designed the multi-step modification of carbon fibers by using the electro-oxidation and -reduction sequential procedure (Scheme 3). Namely, the anodically introduced hydroxyl groups on the suitably oxidized carbon fiber were protected by forming the ether bonds under the electroreductive conditions. The electroreductive protection of hydroxyl groups prevents the undesirable over-oxidation and new hydroxyl groups are introduced by the further electrooxidation of the carbon fiber surface. The resulting carbon fiber is further treated under the electroreductive modification and electrooxidation repeatedly, and the content of the protected hydroxyl groups on the carbon fiber is expected to increase stepwise by the sequential procedure. The sequential introduction of butoxy groups on the carbon fiber was demonstrated by the electrooxidation and the electroreductive modification with 1-bromobutane, and the resulting carbon fibers was evaluated by the measurement of their hydrophilicity, the electrode effects in the electroreduction of acetophenone (**1**) (Table 3), and the surface study by XPS (Fig. 2). The change of the hydrophilicity of the resulting carbon fibers and the peak based on the phenolic hydroxyl groups at 286.8 eV in the C 1s spectrum clearly indicated the introduction

Fig. 2 Photoelectron lines of C 1s and O 1s in a) untreated CF, b) CF-ox., c) CF-mod. Bu, d) CF-mod-ox. and e) CF-mod-mod. Bu.

of hydroxyl groups of the oxidized carbon fibers (entries 2, 4) and alkoxylation by electroreductive modification (entries 3, 5). Remarkable differences were not observed between the O 1s spectra of these carbon fibers. The *dl/meso* ratio of the diol **2** was increased by using the carbon fiber cathode after the oxidation (entries 2, 4), and decreased by using those after the alkoxylation (entries 3, 5). Especially, the hydrophilicity and the increase of the *dl/meso* ratio of **2** supported the fact that the second oxidation of CF-mod. Bu proceeded without the over-oxidation to introduce new hydroxyl groups.

3. 4 Optimization of solvent system for the electrochemical modification

We have attempted the exploitation of new continuous modification method, which enables the successive introduction of the hydroxyl, and the functional groups onto the carbon fiber in one-pot only by alternation of electrodes. In order to perform the electro-oxidation and -reduction sequence in one-pot, it is necessary to find a

Table 4 Electroreductive^{a)} modification of oxidized carbon fiber in several solvents.

Entry	Solvent	Volume (mL)	1-Bromobutane (mmol)	Hydrophilicity of Resulting CF
1	DMF	55	5	Hydrophobic ^{b)}
2	MeCN-H ₂ O (10 : 1)	55	5	Hydrophilic ^{c)}
3	MeCN-H ₂ O (10 : 1)	55	10	Hydrophilic ^{c)}
4	MeCN-H ₂ O (10 : 1)	55	20	Hydrophobic / Hydrophilic ^{d)}
5	MeCN-H ₂ O (3 : 1)	30	5	Hydrophobic ^{b)}

^{a)} The electroreductive modification was carried out in a solution of 1-bromobutane in solvent in the presence of Bu₄NClO₄ (5 mmol). The electricity was 4 F/mol based on 1-bromobutane. ^{b)} Both faces of carbon fiber surface shed a drop of water. ^{c)} Both faces of carbon fiber surface absorbed a drop of water rapidly. ^{d)} One face of carbon fiber surface shed a drop of water, while the other face was absorbed a drop of water.

Fig 3 Plausible mechanism participating of H₂O in electroreductive modification.

common electrolyte for both the electrooxidation and the electroreductive modification. The electrooxidation was usually carried out in MeCN-H₂O (10 : 1) and the electroreductive modification, in DMF. The MeCN-H₂O mixed solvent systems have been tried for the electroreductive modification of the CF-ox. with 1-bromobutane (Table 4). The electroreductive modification was performed in MeCN-H₂O (10 : 1), which is the same solvent system as the electrooxidation, with increasing the added amount of 1-bromobutane as an electrophile (entries 2-4). The hydrophilicity of the carbon fibers was, however, not changed and it indicated that the electroreductive alkoxylation did not proceed efficiently. Interestingly higher content of water was found to be effective to the electroreductive modification. The carbon fiber surface became hydrophobic by the electroreduction in MeCN-H₂O (3 : 1) (entry 5).

The effect of the H₂O containing solvents can be explained by the indirect deprotonation mechanism shown in Fig. 3, while the electroreductive modification usually proceeds in direct mechanism in anhydrous media such as DMF. The hydroxide ions are generated by the electroreduction of water, and react as an electro-generated base with the hydroxyl groups on the carbon fiber to form the anionic species. This indirect deprotonation is probably more effective than the direct deprotonation from the hydroxyl groups on the cathode.

The electrooxidation of untreated carbon fiber in the presence of LiNO₃ was also performed in several solvent system (Table 5). MeCN-H₂O (10 : 1) was usually used in the electrooxidation, however, not effective for the electroreductive modification as mentioned above. The use of aprotic polar solvent such as DMF and DMSO, which were suitable for the electroreductive modification of carbon fibers, were also examined, however, these sol-

Table 5 Electrooxidation^{a)} of untreated carbon fiber in several solvents.

Entry	Solvent	Volume (mL)	Hydrophilicity of Resulting CF
1	MeCN-H ₂ O (10 : 1)	55	Hydrophilic ^{b)}
2	DMF	30	— ^{c)}
3	DMSO	30	Hydrophilic / Hydrophobic ^{d)}
4	MeCN-H ₂ O (3 : 1)	30	Hydrophilic ^{b)}

^{a)} The electrooxidation was carried out in a solution of LiNO₃ (5 mmol) in solvent. The electricity was 3 F/mol based on LiNO₃. ^{b)} Both faces of carbon fiber surface absorbed a drop of water rapidly. ^{c)} The electricity was passivated by the rise of terminal voltage. ^{d)} One face of carbon fiber surface absorbed a drop of water, while the other face was shed a drop of water.

vents were not effective for the electrooxidation of carbon fibers (entries 3, 4). Fortunately, the MeCN-H₂O (3 : 1) mixed solvent, which was found to be effective for the electroreductive modification, was also effective for the electrooxidation of carbon fiber and the hydrophilic carbon fiber was successfully obtained (entry 4).

3. 5 Optimization of supporting electrolytes for the electrochemical modification

The supporting electrolytes were next optimized for the electro-oxidation and -reduction sequence in MeCN-H₂O (3 : 1) (Table 6). In the electrooxidation of carbon fiber surface LiNO₃ was usually used, and in the electroreductive modification, Bu₄NClO₄. Then the mixed salts of LiNO₃ and Bu₄NClO₄ were examined (entry 1). The surface oxidation proceeded, successfully making the surface of carbon fiber hydrophilic, however, the successive electroreductive modification was not achieved and the hydrophobic character which should appear on

Table 6 Optimization of supporting electrolyte system for electrooxidation and electroreductive modification.

Entry	Supporting electrolyte	Hydrophilicity of resulting carbon fiber	
		Electrooxidation ^{a)}	Electroreductive modification ^{b)}
1	LiNO ₃ -Bu ₄ NClO ₄ (1 : 1)	Hydrophilic ^{c)}	Hydrophilic ^{c)}
2	Bu ₄ NNO ₃	Hydrophilic ^{c)}	Hydrophobic / Hydrophilic ^{d)}
3	Bu ₄ NNO ₃ -Bu ₄ NClO ₄ (4 : 1)	—	Partially hydrophilic ^{e)}
4	Bu ₄ NNO ₃ -Bu ₄ NClO ₄ (3 : 2)	—	Hydrophobic / Partially hydrophilic ^{f)}
5	Bu ₄ NNO ₃ -Bu ₄ NClO ₄ (1 : 1)	Hydrophilic ^{c)}	Hydrophobic ^{g)}

^{a)} The electrooxidation was carried out in a solution of supporting electrolytes (5 mmol) in MeCN-H₂O (3:1) (30 mL). The electricity was 3 F/mol based on supporting electrolytes. ^{b)} The electroreductive modification was carried out in a solution of 1-bromobutane (5 mmol) in MeCN-H₂O (3 : 1) (30 mL) in the presence of supporting electrolyte (5 mmol). The electricity was 4 F/mol based on 1-bromobutane. ^{c)} Both faces of carbon fiber surface shed a drop of water. ^{d)} One face of carbon fiber surface shed a drop of water, while the other side absorbed a drop of water. ^{e)} Both faces of carbon fiber surface absorbed a drop of water partially. ^{f)} One face of carbon fiber surface shed a drop of water partially, while the other side absorbed a drop of water. ^{g)} Both faces of carbon fiber surface absorbed a drop of water rapidly.

Scheme 4 Sequential surface treatment of CF under the conditions on 3 F/mol of electrooxidation in MeCN-H₂O (10 : 1) solution (55 mL) of LiNO₃ (5 mmol), b) 4 F/mol electricity of electroreductive modification in the presence of hexanoic anhydride (5 mmol) in DMF solution (50 mL) of Bu₄NClO₄ (5 mmol) and c) THF solution (50 mL) of LAH (5 mmol).

the carbon fiber after alkoxylation of the anodically introduced hydroxyl groups was not observed. It is probably due to relatively low nucleophilicity of the alkoxide ion bearing lithium ion as a counter cation. Most of the alkoxide ions which are formed by the deprotonation of the hydroxyl groups on the CF-ox. under these electroreduction conditions have lithium ions as counter cations, and are less nucleophilic than the alkoxide ions bearing tetrabutylammonium ions. We have next tried Bu₄NNO₃ as a quaternary ammonium salt having NO₃ anion (entry 2). This salt was effective for the electrooxidation of the carbon fiber surface since the resulting oxidized carbon fiber showed high hydrophilicity, but the result of the electroreductive modification of the CF-ox. by using Bu₄NNO₃ was not satisfactory. High concentration of NO₃ anions in the electrolytes enhances the generation of the oxidative NO₃ radicals, which probably prevent the electroreductive modification of the carbon fiber. In order to control the concentration of NO₃ anions in the electrolytes, the mixed electrolytes of Bu₄NNO₃ and Bu₄NClO₄ were used and the mixed ratio was optimized (entries 3-5). Finally the mixed supporting electrolytes system of Bu₄NNO₃-Bu₄NClO₄ (1 : 1) in the mixed solvent of MeCN-H₂O (3 : 1) was found to be effective for both the electrooxidation of the carbon fiber surface and the successive electroreductive alkoxylation of the anodically introduced hydroxyl groups.

3. 6 Electrochemical successive one-pot modification of carbon fibers

By using the optimized electrolyte, Bu₄NNO₃-Bu₄NClO₄ (1 : 1) mixed supporting electrolytes in MeCN-H₂O (3 : 1),

we have successively carried out the electrooxidation (3 F/mol based on Bu₄NNO₃) of the carbon fiber surface and the electroreductive modification (4 F/mol based on 1-bromobutane) in the presence of 1-bromobutane as an electrophile to afford the carbon fiber modified with butoxy groups. Moreover this electro-oxidation and -reduction sequence can be repeated for three times by alternating the polarity of the electrodes with the interval of 1 F/mol. After total 6 F/mol of electricity was passed, one face of the resulting carbon fiber was hydrophobic and the other face showed the hydrophilicity. It probably indicates that the introduction of hydroxyl groups by the electrooxidation proceeds more effectively than the alkoxylation by the electroreduction. In order to confirm the increase of the content of the introduced substituents on the carbon fiber by the successive electrochemical treatment, the electroreductive transformation of the anodically introduced hydroxyl groups to the ester groups by using hexanoic anhydride as an electrophile, further electrooxidation of the protected carbon fiber, and the reduction of the introduced ester groups to hydroxyl groups by using LAH were examined (Scheme 4). The observation of hydrophilicity and the surface study by XPS of the resulting carbon fibers clearly indicated the introduction of ester groups by the electroreductive modification and the recovery of hydroxyl groups by the treatment with LAH. Additionally the electroreduction of acetophenone (**1**) by using the LAH-reduced CF-mod-ox. as a working electrode gave the highest *dl/meso* ratio (5.4) of diol **2** in our research, and this result indicated the increase of the content of the

introduced hydroxyl groups on the carbon fiber.

4 Conclusion

The correlation between the supplied electricity in the electrooxidation and the relative amount of the introduced hydroxyl groups on the carbon fiber surface was investigated, and it was confirmed that the amount of hydroxyl groups on the carbon fiber increased with an increase in electricity until about 5 F/mol based on LiNO_3 but further electrooxidation resulted in the decrease of the hydroxyl groups by the over-oxidation. Then we designed the sequential surface modification process of the carbon fiber by using the electrooxidation and electroreductive modification repeatedly. By using the electro-oxidation and -reduction sequential procedure, the stepwise increase of the introduced content of the substituents on the carbon fiber surface was expected without the over-oxidation. Moreover, we have attempted the exploitation of the successive modification method of the carbon fiber in one-pot by alternating the polarity of the electrodes, and optimized the electrolyte for this purpose. In the optimized electrolyte, $\text{MeCN-H}_2\text{O}$ mixed solvent (3 : 1) containing the mixed supporting electrolytes of $\text{Bu}_4\text{NNO}_3\text{-Bu}_4\text{NClO}_4$ (1 : 1), the successive electrooxidation and electroreductive modification of the carbon fiber in one-pot was achieved to give the carbon fiber having higher content of the hydroxyl or alkoxy groups.

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