— Article —

Preparation of the Modified Platinum Electrodes Bearing the Alkali Metal Ion - Crown Ether Complexes as Mediatory Centers and Their Application to the Electroreduction of Methyl Decanoate

Manabu ISHIFUNE,* Hajime YAMASHITA, Daisuke HASHIMOTO, Hiroshi KANESEI, and Yoshimi KAKUTANI

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University (3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan)

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The modified platinum electrodes having complexes of sodium with crown ether type ligands were prepared and utilized in the electroreduction of methyl decanoate (**1**) in the presence of *t*-BuOH as a proton donor and Bu₄NClO₄ as a supporting electrolyte. The product yield by using the modified platinum electrode having the complex of lithium or sodium ion with the monomeric ligand LA (*MPt(A)-Na*) was 46%. The use of the modified platinum electrodes having the complex of sodium ion with the polymeric ligands LB (*MPt(B)-Na*) or LC (*MPt(C)-Na*) gave the reduced product in 52% or 47% yield respectively. Durability of the electrodes, *MPt(A)-Na* and *MPt(B)-Na*, under the electroreduction conditions was not so high, however, the activity of the electrodes was found to be recovered by the re-complexation of sodium ion with the ligand on the surface of the used modified electrodes. The durability of the electrode *MPt(C)-Na* was satisfactory to use repeatedly, and the use of *MPt(C)-Na* as a cathode and NaClO₄ instead of Bu₄NClO₄ as a supporting electrolyte gave the reduced product in 69% yield. Moreover, using the modified electrodes in the presence of anodically dissolved magnesium ion the reduced product was obtained in >90% yield.

Key Words : Electroreduction, Aliphatic Ester, Modified Electrode, Alkali Metal Ions, Crown Ethers

1 Introduction

We have already achieved the electroreduction of methyl decanoate (**1**), which is known to be a hardly electroreductive compound because of its highly negative reduction potential (~ -3.0 V vs. SCE) in comparison with that of ketones or aldehydes, in the presence of *t*-BuOH as a proton source and LiClO₄ as a supporting electrolyte.¹⁻⁷⁾ Using platinum anode and cathode or using a platinum anode and a magnesium cathode, the electroreduction of **1** gave the coupling product, 2-alkoxytetrahydrofuran **4**.⁸⁾ The formation of acetal **4** is due to the coupling reaction between the alkoxide anion **2** generated by the electroreduction of **1** on the cathode and THF cation **3** produced by the oxidation of THF as a solvent on the platinum anode (Scheme 1).

In this electroreduction of the ester **1**, the electron transfer to **1** from cathode is probably mediated by the electrogenerated active reductant.⁹⁻¹¹⁾ We have demonstrated that the use of supporting electrolytes containing alkali metal ions such as LiClO₄ is very important to promote the electroreduction of **1**. The active reductant, probably the alkali metal (0), is probably generated by the electroreduction of the alkali metal ion from the supporting electrolyte and its life time in the electrolysis solution seems to be considerably short. In fact by the complexation of alkali metal ions with the crown ether type ligands, the yield of the reduced product **4** was increased in comparison with that obtained under the conditions using alkali metal salts.⁸⁾ Therefore, in order

to enhance the reaction efficiency it is promising to fix the mediatory centers on the electrode surface and to restrict the diffusion of the mediators into the electrolysis solution.

Electrodes chemically modified with redox groups are utilized in the processes of electrochemical and photoelectrochemical catalysis. In particular, immobilized redox groups can function as an electron transfer mediator between substrates and the electrode.¹²⁾ More recently the heme peptide multilayer-modified electrodes has been reported as an enzyme model electrode.¹³⁾ The platinum/poly (methyl violet) chemically modified electrode was also reported to have excellent catalytic activi-

Scheme 1 Paired electrolysis system of the combination between the cathodic reduction of methyl decanoate and the anodic oxidation of THF (solvent).

ty for the oxidation of cysteine and methionine.¹⁴⁾ Thus, modifying the surface of an electrode with a redox mediator is a well-established strategy for achieving wider applicability of electrochemical reactions. In this study we have prepared the modified electrode having the complexes of alkali metal ion with monomeric or polymeric crown ether type ligands as mediatory centers, and proposed new electroreduction systems using the modified electrodes. Additionally we have investigated the effect of magnesium ion as an electron transfer catalyst in this electroreduction system.

2 Experimental

2.1 General

The constant current electrolysis was carried out with a Takasago Gp-0-52 DC power supply. The supplied electricity was counted by a Hokuto Denko Coulomb Amperehour Meter HF-201. ¹H NMR or ¹³C NMR spectra were recorded on a JEOL-GSX-270 (270 MHz) FT-NMR or a Varian OXORD NMR 300 (300 MHz) FT-NMR spectrometer and chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. IR spectra were obtained on a Jasco FT-IR-470 Plus spectrometer. MS spectra were obtained on a JEOL-JMS700 spectrometer. Gel permeation chromatography (GPC) analyses were carried out on a Hitachi L-6000 high performance liquid chromatograph, a L-3350 RI detector and a Shodex[®] GPC A-803 column. Tetrahydrofuran was used as an eluent with a flow rate of 1.0 mL/min, and molecular weight values are relative to the polystyrene standards (Shodex[®] STANDARD (SM-105) polystyrene). X-ray photoelectron spectroscopy for chemical analyses (ESCA) were acquired using a Shimadzu ESCA 3200 with a Mg X-ray source under vacuum of 10^{-5} – 10^{-7} mmHg.

2.2 Materials

Tetrahydrofuran (THF) was distilled from sodium - benzophenoneketyl under an argon atmosphere. *N,N*-Dimethylformamide (DMF) was distilled in the presence of a small amount of water and benzene to remove dimethylamine and formaldehyde, and distilled again under reduced pressure. α -Methylstyrene and styrene were distilled in the presence of a trace amount of hydroquinone under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Toluene was shaken with *conc.* H₂SO₄ until decolorized, washed with NaOHaq and water, dried over CaCl₂, and distilled from sodium - benzophenoneketyl under an argon atmosphere. *t*-BuOH was distilled under an argon atmosphere after reflux in the presence of a trace amount of sodium metal to remove residual water. Methyl decanoate as a starting material was distilled under reduced pressure. Platinum as an electrode material was polished and washed with water. Magnesium ingot was cut into rods (Φ = 9 mm, length = 40 mm) for electrodes. Other reagents were commercially available and used without further purification.

2.3 Synthesis of 4'-(Triethoxysiloxy) methylbenzo-15-crown-5, the monomeric ligand LA

The monomeric ligand LA was synthesized from 3,4-

Scheme 2 Preparation of monomeric ligand LA.

dihydroxybenzaldehyde according to Ungaro's procedure,¹⁵⁾ and the synthetic route and yields were shown in Scheme 2.

2.3.1 4'-(Hydroxymethyl)benzo-15-crown-5 (5)

To a well-stirred solution of 10 mmol of 4'-formylbenzo-15-crown-5^{16, 17)} in 60 mL of ethanol was added 0.6 g of NaBH₄. The reaction mixture became homogeneous after several minutes. After stirring for 24 h at room temperature the solution was poured into 60 mL of water, neutralized with dilute acetic acid, and extracted with chloroform. After washing with saturated NaCl_{aq} and drying over Na₂SO₄, chloroform was evaporated and oily residue was allowed to crystallize. The solid was suspended in diethyl ether and filtered to afford **5** (yield 56%): IR (CHCl₃) 3385, 3013, 2925, 2873, 1057, 808 cm⁻¹; ¹H NMR (CDCl₃) δ 3.45 (br, 1H, OH), 3.60–4.20 (m, 16H), 4.58 (s, 2H), 6.89–6.90 (m, 3H).

2.3.2 4'-(Triethoxysiloxy)methylbenzo-15-crown-5 (LA)

To a solution of 3.5 mmol of 4'-(Hydroxymethyl)benzo-15-crown-5 (**5**) in 10 mL of benzene was added 4 mmol of pyridine and 4 mmol of triethoxychlorosilane was added dropwise. After stirring for 3 h at room temperature, the solution was filtered and filtered solid was washed with benzene. The combined filtrates were evaporated until no benzene could be detected. The oily residue was purified by column chromatography (silica gel, 10:1 chloroform/methanol) to give 4'-(triethoxysiloxy)methylbenzo-15-crown-5 (**LA**): IR (neat) 3397, 2974, 2884, 1514, 1432, 1364, 1267, 1168, 1078 cm⁻¹; ¹H NMR (CDCl₃) δ 1.19 (t, 9H, *J* = 6.9 Hz), 3.70–3.76 (m, 8H), 3.80 (q, 6H, *J* = 6.9 Hz), 3.86–3.91 (m, 4H), 4.08–4.14 (m, 4H), 4.74 (s, 2H), 6.78–6.93 (m, 3H); HRMS calcd. for C₂₁H₃₆O₉Si 460.2129, found: 460.2161.

2.4 Synthesis of polymeric ligands LB by the anionic copolymerization of styrene (St) with 4'-vinylbenzo-15-crown-5 (VB15C5) (Scheme 3)

A solution of di-anions of α -methylstyrene (cumyl potassium) tetramer was prepared by keeping a 0.5 mol/L solution of α -methylstyrene in THF in contact with a potassium mirror for 24 h at room temperature (the ratio K : α -methylstyrene = 1 : 2^{18–20)}). Both solutions must be kept -78°C , to a vigorously stirred 4 mL (2 mmol) of solution of di-anions of potassium tetramer of α -methylstyrene in THF was added a solution of 4 mmol of styrene (St) with 4 mmol of 4'-vinylbenzo-15-crown-5 (**VB15C5**) (prepared in our previous research⁸⁾) in 16 mL of THF. After the polymerization time for 2 h at -78°C the polymerization mixture was added to 4 mmol of triethoxychlorosilane as a terminator. Until living

Scheme 3 Preparation of the polymeric ligands LB.

anions in polymer end-group were inactivated, the reaction mixture was vigorously stirred at room temperature. The reaction mixture was poured into a large amount of hexane, and the resulting precipitate was filtered and dried *in vacuo* at room temperature. The crude polymer was purified by reprecipitation from benzene into hexane to give the polymeric ligand LB.^{20–22} The number average molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were determined by GPC to be *ca.* 17400 and 1.01 respectively. The content of vinylbenzo-15-crown-5 units in the copolymer was determined by ¹H NMR to be 40%.

2. 5 Synthesis of the polymeric ligands LC

The polymeric ligand LC was synthesized by radical copolymerization of styrene (St), 4'-vinylbenzo-15-crown-5 (VB15C5) and *p*-triethoxysiloxystyrene (TEST) (Scheme 4).

2. 5. 1 Preparation of *p*-triethoxysiloxystyrene (TEST) monomer

To the solution of 10 mmol of *p*-hydroxystyrene^{23, 24} and 12 mmol of imidazole in 10 mL of dry DMF was added the solution of 12 mmol of triethoxysilane in 10 mL of dry DMF at 0 °C under an argon atmosphere. After stirring for 5 h at room temperature, the reaction mixture was poured into ice water. The aqueous solution was extracted with diethyl ether, and the organic layer was washed with saturated NaCl aq. and 5% NaHCO₃ aq., and then dried over anhydrous MgSO₄. The residue obtained by evaporation of the solvent was distilled under reduced pressure (90 °C / 2 mmHg) in the presence of a trace amount of 4-*t*-butylcatechol to give *p*-triethoxysiloxystyrene (TEST) (yield 58%): IR (neat) 2977, 2928, 2894, 1629, 1606, 1509 cm⁻¹; ¹H NMR (CDCl₃) δ 1.24 (t, 9H, *J* = 7.2 Hz), 3.91 (q, 6H, *J* = 7.2 Hz), 5.14 (dd, 1H, *J* = 0.6 Hz, 10.8 Hz), 5.62 (dd, 1H, *J* = 0.6 Hz, 17.7 Hz), 6.65

Scheme 4 Preparation of the polymeric ligand LC.

(dd, 1H, *J* = 10.8 Hz, 17.7 Hz), 6.94–7.00 (m, 2H), 7.24–7.34 (m, 2H); HRMS calcd. for C₁₄H₂₂O₄Si 282.1287, found: 282.1280.

2. 5. 2 Radical copolymerization of styrene (St), 4'-vinylbenzo-15-crown-5 (VB15C5), and *p*-triethoxysiloxystyrene (TEST)

A solution of styrene (St) (1 mmol), 4'-vinylbenzo-15-crown-5 (VB15C5) (1 mmol), *p*-triethoxysiloxystyrene (TEST) (1 mmol), and AIBN (0.03 mmol) as an initiator in 3 mL in dry toluene was placed in a glass ampoule under an argon atmosphere. The ampoule was degassed by repeating freeze-evacuate-thaw cycles several times, and sealed under vacuum. The polymerization was carried out in water bath at 70 °C for 36 h. After a small amount of toluene was removed, the reaction mixture was poured into a large amount of hexane to precipitate the polymer. The resulting precipitate was filtered and dried *in vacuo* at room temperature. The crude polymer was purified by reprecipitation from benzene into hexane to give the polymeric ligand LC. The molecular weight ($\bar{M}_n$) and $\bar{M}_w/\bar{M}_n$ of the ligand LC were *ca.* 7750 and 1.75 respectively. And the contents of vinylbenzo-15-crown-5 units and triethoxysiloxystyrene units in the resulting copolymer were determined by ¹H NMR to be 38% and 26% respectively.

2. 6 Modification of platinum electrode with crown ether ligands and coordination of alkali metal ions^{12, 25}

The crown ether ligands were modified on the surface of platinum electrodes with the siloxane bonding between the anodically oxidized platinum electrode (Pt/PtO) and triethoxysilyl groups in the crown ether ligands (LA, LB, and LC). And sodium ion was coordinated by the crown ether ligand on the platinum electrode (Scheme 5). The plausible structures of these modified platinum electrodes (MPt(A)-Na, MPt(B)-Na, MPt(C)-Na) were illustrated in Fig. 1.

Scheme 5 Preparation of the modified platinum electrodes having the complexes of sodium ions with the crown ether type ligands.

Fig. 1 Modified platinum electrodes having the complex of sodium ion with crown ether type ligand.

2. 6. 1 Surface oxidation of platinum electrode

Mirror-polished platinum electrode (plate, $0.3 \times 20 \times 20$ mm) anodized for 10 min. at +1.9 V vs. Ag/Ag⁺ in 1 mol/L H₂SO₄aq were cycle between hydrogen and oxygen discharge until the characteristic platinum wave pattern was observed.²⁶⁾ The electrodes were then potentiostated at 1.1 V for 5 min., washed thoroughly with distilled water, and vacuum-dried at 50 °C for 20 min.

2. 6. 2 Modification of crown ether type ligands (LA, LB, LC) on the surface of oxidized platinum electrode and fixation of alkali metal ions

The surface oxidized platinum electrode (Pt/PtO) was washed three times with dry toluene under an argon atmosphere. The electrode was dipped in the 8% of dry toluene solution of 4'-(triethoxysiloxy)methylbenzo-15-crown-5 (LA) for 5 min. The modification of polymeric ligands LB, LC on the surface of platinum electrodes were carried out by dipping the electrodes in the 8% of toluene solution of polymeric ligands for 24 h. The resulting silanized (modified) platinum electrodes (MPt(A), MPt(B), MPt(C)) were washed six times with dry toluene and twice with dry THF. After being dipped in THF solution of NaClO₄ for 30 min, the platinum electrode were washed with dry THF under sonication of ultrasound (42-50 Hz) overnight. The resulting electrodes coordinated sodium ion (MPt(A)-Na, MPt(B)-Na, MPt(C)-Na) were further washed several times with dry THF and dried *in vacuo*.

2. 7 Electroreduction of methyl decanoate (1) using the modified platinum electrode

In an undivided electrolysis cell equipped with the

modified platinum cathode and an untreated platinum anode were placed anhydrous 10 mmol of Bu₄NClO₄ as a supporting electrolyte and 20 mL of dry THF under an argon atmosphere. To the reaction solution was added 2 mmol of methyl decanoate (1) and 12 mmol of distilled *t*-BuOH as a proton donor. Seven F/mol of electricity based on 1 was passed under the condition of constant current (50 mA) at *ca.* 5 °C. The reaction mixture was poured into 100 mL of saturated NH₄Cl aq. After the aqueous solution was extracted with diethyl ether (50 mL $\times$ 3), the precipitated supporting electrolyte was filtered. The combined organic layer was washed with 0.5 N HCl, saturated NaHCO₃ aq and NaCl aq, and then dried over anhydrous MgSO₄. The residue obtained by evaporation of the solvent was distilled by a glass tube oven under reduced pressure (95-105 °C / 2 mmHg) to give the reduced product, 2-decanoyltetrahydrofuran (4): IR (neat) 2925, 1460, 1345, 1095, 1040 cm⁻¹; ¹H NMR (CDCl₃) δ 0.85 (t, 3H, *J* = 6.7 Hz), 1.14-1.36 (m, 14H), 1.42-1.58 (m, 2H), 1.70-2.06 (m, 4H), 3.33 (td, 1H, *J* = 6.6 Hz, 9.6 Hz), 3.61 (td, 1H, *J* = 6.9 Hz, 9.6 Hz), 3.78-3.71 (m, 2H), 5.08 (dd, 1H, 1.8 Hz, 4.2Hz); ¹³C NMR (CDCl₃) 14.12, 22.67, 23.51, 26.17, 29.31, 29.42, 29.56, 29.60, 29.73, 31.89, 32.30, 66.75, 67.32, 103.74; FAB-HRMS calcd. for C₁₄H₂₈O₂ (M + H) 229.2167, found: 229.2171.

3 Results and Discussion

3. 1 Surface study of the modified platinum electrode by X-ray photoelectron spectra (ESCA)

The compositions of chemical elements on the surface

Fig. 2 X-ray photoelectron spectroscopy (ESCA) of the modified platinum electrodes having sodium ion with monomeric ligand LA (MPt(A)-Na) and polymeric ligand LB (MPt(B)-Na).

of the resulting modified platinum electrodes (*MPt(A)-Na*, *MPt(B)-Na*, *MPt(C)-Na*) were characterized by ESCA. The composition of chemical elements on the surface of the modified platinum electrodes having the complexes of sodium ion with the monomeric ligand **LA** (*MPt(A)-Na*) and polymeric ligand **LB** (*MPt(B)-Na*) were shown in Fig. 2. Since the peaks of C 1s, O 1s, and Si 2p in the spectra of the modified electrodes (*MPt(A)-Na*, *MPt(B)-Na*) were strongly observed at *ca.* 286.5 eV, 533 eV, and 103 eV respectively, the monomeric and polymeric ligands **LA** and **LB** are confirmed to be fixed on the surface of the oxidized platinum. Additionally the Na 1s band was also observed at *ca.* 1065–1072 eV. This result indicates that sodium ions were coordinated by the crown ether ligands **LA** and **LB** on the surface of platinum electrodes since the Na 1s band was not detected in the untreated platinum. ESCA of the modified platinum electrode having the complexes of sodium ion with the polymeric ligand **LC** (*MPt(C)-Na*) was also performed with etching operation, which was carried out by the method of scraping surface by Ar Ion Gun (2.0 kV, 20 mA, 0.1 min). At the outer layer, C 1s, O 1s and Si 2p peaks were observed but Pt 4f spectra was relatively weak. After the etching operation, the intensity of C 1s, O 1s, and Si 2p peaks were relatively weakened but the Pt 4f peak was increased. The Na 1s peak were also observed at *ca.* 1072 eV after first etching operation was carried out. These results indicated that the polymeric ligand **LC** was immobilized to the surface of platinum electrode and sodium ions were fixed.

3. 2 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with the monomeric ligand **LA** (*MPt(A)-Na*)

It has been already found that the addition of the complex of sodium ion with 15-crown-5 in the electroreduction of methyl decanoate (**1**) was highly effective to promote the electroreduction in comparison with the addi-

tion of the complex of lithium ion with 15-crown-5.⁸⁾ Sodium ion was then fixed on the surface of platinum electrode by the coordination with the monomeric ligand **LA**. Table 1 shows the results of the electroreduction of **1** using the modified platinum electrode having the complex of sodium ion with the monomeric ligand **LA** (*MPt(A)-Na*). The reduced product **4** was given in 29% by using untreated platinum anode and cathode in the presence of 0.05 equiv. (based on **1**) of the complex of sodium ion with 15-crown-5 (entry 3). The use of the modified platinum electrode (*MPt(A)-Na*) as a cathode and an untreated platinum electrode as an anode resulted in 17% increase of the product yield (46%) in comparison with the yield under the condition of entry 3 (entry 4). The second use of the modified platinum electrode (*MPt(A)-Na*) after washing with THF gave the reduced product **4** in only 26% yield (entry 5). These results indicated that sodium ion was released from the coordination site on the electrode during the electroreduction. However, the activity of the modified electrode was found to be recovered by the re-complexation of sodium ion with the monomeric ligand **LA** on the surface of the used modified platinum electrode, affording the reduced product **4** in 45% yield (entry 6). Therefore, the structure of ligand **LA** fixed on the platinum surface was probably not changed under the electroreduction conditions.

The structure of ligand and behavior of sodium ion were also conformed by ESCA. The ESCA data on the outer layer of used modified platinum electrode (*MPt(A)-Na*) show the presence of the elements included in the monomeric ligand **LA** (Fig. 3). Namely, the strength of C 1s and O 1s peaks relative to Pt 4f peak of the modified platinum electrode (*MPt(A)-Na*) did not change after using for the electroreduction. On the other hand, the strength of Na 1s peak of the used modified electrode remarkably decreased.

Table 1 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with the monomeric ligand **LA** (*MPt(A)-Na*)^a.

Entry	Cathode ^b	Additive (equiv. based on 1)	Yield ^c of 4 , %
1	Untreated Pt	non	trace
2	Untreated Pt	NaClO ₄ (0.05)	19
3	Untreated Pt	Na ⁺ -15C5·ClO ₄ ⁻ (0.05)	29
4	MPt(A)-Na (1st)	non	46
5	MPt(A)-Na (2nd)	non	26
6	MPt(A)-Na (re-complexation)	non	45
7	MPt(A)-Na (1st)	NaClO ₄ ^b (5)	46

^aThe electroreduction was carried out in THF in the presence of *t*-BuOH (6 equiv. based on **1**) as a proton donor using an untreated platinum as an anode and the modified platinum electrode having the complex of sodium ion with the monomeric ligand **LA** (*MPt(A)-Na*) as a cathode. The electricity was 7 F/mol based on **1**.

^bTo the reaction solution was added 5 equiv. based on **1** of NaClO₄ as a supporting electrolyte.

^cDetermined by ¹H NMR.

Fig. 3 X-ray photoelectron spectra of the surfaces of the modified electrodes *MPt(A)-Na* before and after using for the electroreduction of **1**.

Moreover the re-complexation of sodium ion with the coordination sites on the surface of electrode was attempted by providing sodium ion from a supporting electrolyte during the electroreduction. Although 10 mmol (5 equiv. based on **1**) of NaClO_4 was used as a supporting electrolyte, the yield of product **4** (46%) was not changed in comparison with that obtained under the conditions of entry 4 (entry 7). This result probably indicated that the re-complexation of sodium ion could not proceed on the negatively potentialized electrode. The modified platinum electrode having the complex of sodium ion with monomeric ligand **LA** (*MPt(A)-Na*) was high, however endurance of the modified platinum electrode (*MPt(A)-Na*) was not satisfactory.

3. 3 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with polymeric ligand **LB** (*MPt(B)-Na*)

The electroreduction of methyl decanoate (**1**) was carried out by using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LB** (*MPt(B)-Na*) as a cathode and an untreated platinum electrode as an anode in the presence of Bu_4NClO_4 as a supporting electrolyte and the results were summarized

in Table 2. The reduced product **4** was obtained in 41% yield by using untreated platinum anode and cathode in the presence of 0.05 equiv. (based on **1**) of the complex of sodium ion with poly(vinylbenzo-15-crown-5-co-styrene), which was prepared by the radical copolymerization of vinylbenzo-15-crown-5 (**VB15C5**) with styrene (**St**) using AIBN as an initiator and complexation of alkali metal ions (entry 1).⁸⁾ Using the modified platinum electrode *MPt(B)-Na*, the electroreduction gave the reduced product **4** in 52% yield (entry 2). The increase of the yields observed between entries 1 and 2 indicated high efficiency of the modified platinum electrode *MPt(B)-Na* to promote the electroreduction of **1**. Moreover the effectiveness of the modified platinum electrode *MPt(B)-Na* in this electroreduction system was higher than that of modified platinum electrode having complex of sodium ion with monomeric ligand **LA** (*MPt(A)-Na*). The second use of modified platinum electrode *MPt(B)-Na* gave the reduced product **4** in 37% yield (entry 3). The re-complexation treatment of sodium ion onto the modified platinum electrode *MPt(B)-Na* was unexpectedly ineffective to recover the activity of the modified electrode, and the reduced product **4** was obtained only 38% yield (entry

Table 2 Electroreduction of methyl decanoate (**1**) using modified platinum electrode having the complex of sodium ion with the polymeric ligand **LB** (*MPt(B)-Na*)^a.

Entry	Cathode	Additive ^b	Yield ^c of 4 , %
1	Untreated Pt	Na^+ -poly(VB15C5-co-St)· ClO_4^- ^d	41
2	<i>MPt(B)-Na</i> (1st)	non	52
3	<i>MPt(B)-Na</i> (2nd)	non	37
4	<i>MPt(B)-Na</i> (re-complexation)	non	38

^aThe electroreduction was carried out in THF in the presence of *t*-BuOH (6 equiv. based on **1**) as a proton donor using a untreated platinum as an anode and the modified platinum electrode as a cathode having the complex of sodium ion with the polymeric ligand **LB** (*MPt(B)-Na*). The electricity was 7 F/mol based on **1**.

^bTo the reaction solution was added 0.05 equiv. based on **1** of sodium ion.

^cDetermined by ¹H NMR.

4). These results probably indicated that a part of the polymeric ligand **LB** was peeled off from the surface of platinum electrode during the electroreduction. The structure of the fixed polymeric ligand **LB** with siloxane bonding must not be affected under the electroreduction conditions since the monomeric ligand **LA** on the electrode was unchanged under the electroreduction conditions. Therefore, it is plausible that a part of the polymeric ligand **LB** is coated over the surface of platinum electrode as the polymer film only by physical adsorption without siloxane bonding. On the other hand the complex of sodium ion with the polymeric ligand **LB** fixed by siloxane bonding on the platinum electrode surface remained to be unchanged during the electroreduction.

3. 4 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC** (*MPt(C)-Na*)

In order to improve the durability of the modified platinum electrode it has been attempted to modify the polymeric ligand film on the surface of a platinum electrode. We have designed and prepared a new type polymeric ligand **LC** having a lot of triethoxysilyl groups in the side chain as functional groups to be modified on the surface of platinum electrode. The polymeric ligand **LC** could be fixed on the surface of the oxidized platinum electrode by several siloxane bonds. We have succeeded in preparation of the modified platinum electrode having high durability under the conditions of electroreduction of methyl decanoate (**1**). Table 3 shows the results of the electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC**, *MPt(C)-Na*, in the presence of Bu_4NClO_4 as alkali metal ion free supporting electrolyte. Using the modified platinum electrode *MPt(C)-Na* as a cathode and an untreated platinum electrode as an anode afforded the reduced product **4** in 47% yield (entry 1). In the second use of the modified platinum electrode *MPt(C)-Na* after washing with THF, the yield of the reduced product **4** (46%) was unchanged (entry 2). The further use of this modified electrode still

showed enough reactivity, and the reduced product **4** was given in 40% yield (entry 3). After re-complexation of sodium ion with the coordination sits on the used modified platinum electrode, the electroreduction of **1** proceeded to afford the reduced product **5** in 49% yield (entry 4). These results indicated that the modified platinum electrode *MPt(C)-Na* had high durability under the electroreduction conditions. The modified platinum electrode *MPt(C)-Na* was more effective to promote the electroreduction of **1** affording **4** than other modified platinum electrodes which were having the complexes of sodium ion with monomeric ligand **LA** (*MPt(A)-Na*) and polymeric ligand **LB** (*MPt(B)-Na*).

3. 5 Additive effect of sodium ion and anodically dissolved magnesium ion in the electroreduction of methyl decanoate (**1**) using the modified platinum electrode (*MPt(B)-Na*, *MPt(C)-Na*)

The preliminary results about the additive effect of magnesium ion into the electroreduction system of aliphatic esters **1** were already discussed in our previous research.⁸⁾ The addition of the anodically dissolved magnesium ion into the electrolyte containing NaClO_4 (5 equiv. based on **1**) and its complex with 15-crown-5 (0.05 equiv.) promoted the electroreduction of **1** affording the reduced product **4**. The additive effect of the anodically dissolved magnesium ion was then investigated in the electroreduction system using the modified platinum electrodes (Scheme 6, Table 4). The electroreduction of **1** was carried out in the presence of NaClO_4 instead of Bu_4NClO_4 as a supporting electrolyte to maintain enough conductivity of the electrolyte.⁸⁾ A solution of NaClO_4 as a supporting electrolyte in THF was electrolyzed in undivided electrolysis cell equipped with magnesium as

Scheme 6 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode in the presence of anodically dissolved magnesium ions.

Table 3 Electroreduction of methyl decanoate (**1**) using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC** (*MPt(C)-Na*)^a.

Entry	Cathode	Anode	Additive ^b	Yield ^c of 4 , %
1	<i>MPt(C)-Na</i> (1st)	Untreated Pt	non	47
2	<i>MPt(C)-Na</i> (2nd)	Untreated Pt	non	46
3	<i>MPt(C)-Na</i> (3rd)	Untreated Pt	non	40
4	<i>MPt(C)-Na</i> (re-complexation)	Untreated Pt	non	49

^aThe electroreduction was carried out in THF in the presence of *t*-BuOH (6 equiv. based on **1**) as a proton donor using an untreated platinum anode and the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC** (*MPt(C)-Na*). The electricity was 7 F/mol based on **1**.

^bTo the reaction solution was added 0.05 equiv. based on **1** of sodium ion.

^cDetermined by ¹H NMR.

Table 4 Additive effect of anodically dissolved magnesium ion in the electroreduction of methyl decanoate (**1**) using the modified platinum electrode (*MPt(B)-Na*, *MPt(C)-Na*) in the presence of NaClO₄ as a supporting electrolyte^a.

Entry	Cathode	Pre-electrolysis ^b anodically dissolved Mg ²⁺ based on 1	Yield ^c of 4 , %
1	Untreated Pt	—	11
2	Untreated Pt	0.75	43
3	<i>MPt(B)-Na</i> (1st)	—	34
4	<i>MPt(B)-Na</i> (1st)	0.75	90
5	<i>MPt(C)-Na</i> (1st)	—	69
6	<i>MPt(C)-Na</i> (1st)	0.75	96

^aThe electroreduction was carried out in the THF in the presence of *t*-BuOH (6 equiv. based on **1**) as a proton donor and NaClO₄ as a supporting electrolyte using an untreated platinum electrode as an anode and the modified platinum electrode as a cathode (*MPt(B)-Na*, *MPt(C)-Na*). The electricity was 7 F/mol based on **1**.

^bThe pre-electrolysis was carried out using magnesium anode and cathode before addition of **1** and *t*-BuOH. After 300 C of electricity was passed, *ca.* 0.75 equiv. based on **1** of magnesium ion was anodically dissolved.

^cDetermined by ¹H NMR.

an anode and a cathode to dissolve *ca.* 0.75 equiv. (based on **1**) of magnesium ion. After 300 C of electricity was passed, the magnesium electrodes were replaced with the untreated platinum as an anode and the modified platinum electrode as a cathode. The ester **1** and *t*-BuOH as a proton donor were then added, and 7 F/mol (based on **1**) of electricity was passed. The reduced product **4** was obtained in 11% yield without the anodically dissolved magnesium ion by using untreated platinum anode and cathode (entry 1), while in the presence of the anodically dissolved magnesium ion **4** was formed in 43% yield (entry 2). Under the conditions using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LB** (*MPt(B)-Na*), the effect of magnesium ion was remarkable. Namely, the yield of **5** was much increased in the presence of the anodically dissolved magnesium ion (entry 4, yield 90%) in comparison with that without magnesium ion (entry 3, yield 34%). The reduced product **4** was obtained in 69% yield by using the modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC** (*MPt(C)-Na*) (entry 5). This result was indicated that addition of NaClO₄ as a supporting electrolyte was effective to promote the electroreduction of **1**. Finally the electroreduction of **1** gave the reduced product **4** in 96% yield by using the modified platinum electrode (*MPt(C)-Na*) in the presence of anodically dissolved magnesium ion, and starting material **1** was not detected (entry 6).

4 Conclusion

We have successfully achieved the fixation of the mediatory systems on the surface of platinum electrode by using the technique of the chemical modification with alkali metal ion - crown ether complexes. That is, by using the platinum electrode chemically modified with the complex of sodium ion with the crown ether type ligands, the electroreduction of hardly electroreducible

aliphatic esters proceeded to afford the reduced acetals. Considering a catalytic amount of sodium ion was fixed on the surface of platinum electrode, it is plausible that sodium ion on the surface of electrode is smoothly electroreduced on the cathode to give sodium metal (0) as an active reductant. This electrogenerated sodium metal seems to have unusually high reactivity since sodium metal could not reduce the aliphatic esters under usual non-electrochemical reaction conditions. The modified platinum electrode having the complex of sodium ion with the polymeric ligand **LC** was found to have enough durability under the electroreduction conditions to use repeatedly. Moreover, the addition of the anodically dissolved magnesium ion in the electroreduction system using the modified platinum electrode was remarkably effective to promote the electroreduction of aliphatic esters and reduced product was obtained in excellent yield. The role of the anodically dissolved magnesium ion remains to be established, however, it is plausible that the reduction potential of aliphatic ester is positively shifted by the coordination of magnesium ion as a Lewis acid to the ester.^{27, 28)} The experimental observation that the reaction suspension containing the anodically dissolved magnesium ion became homogenous as soon as the addition of aliphatic esters also indicated the complexation of magnesium ion with the esters.

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