Poly (*N*-Trihydroxyl Alkane Substituted Pyrrole) Film Coated Electrodes for Catalytic Hydrogenation

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1 INTRODUCTION

Incorporation of catalytic metals in conductive polymer films on electrode can be conveniently achieved and the application as an electrochemical catalysis electrode is expected¹⁾. We have previously reported the palladium incorporated poly [*N*-(5-hydroxypentyl substituted pyrrole)] film electrode (P5HPy)²⁾. However, this film electrode was not fully satisfied in catalytic function. Furthermore the construction of excellent and stable film electrodes is necessary. In particular, it is important to secure space for the movement of substrates in polymer film. We synthesized the *N*-alkane substituted pyrrole monomers **1a** and **1b**, which are linked a bulky molecular at a carbon chain terminal. In this paper, we report the preparation and properties of new poly (*N*-trihydroxyl alkane substituted pyrrole) film electrodes **2a** and **2b** for electrocatalytic hydrogenation.

2a: $n = 2$

2b: $n = 5$

2 EXPERIMENTAL

As shown in Scheme 1 the trihydroxyl alkane substituted pyrrole monomers **1a** and **1b** were synthesized by ordinary method³⁾. The monomers were purified by column chromatography using AcOEt / *n*-hexane as the eluent.

Scheme 1

NMR and IR spectroscopic data of the monomers followed; **1a**: ¹H NMR (270 MHz, DMSO-*d*₆) δ 3.31~3.35 (m, 8H, $\equiv$ C-CH₂-O-), 3.56 (t, 2H, $J=5.6, 5.3$, >N-CH₂-CH₂-O-), 3.99 (t, 2H, $J=5.6, 5.3$, >N-CH₂-CH₂-O-), 4.16~4.19 (m, 3H, OH), 5.96 (t, 2H, $J=2.0, 2.3$, PyH_{3,4}), 6.74 (t, 2H, $J=2.0, 2.3$, PyH_{2,5}); IR (neat) ν 3379, 2929, 2883, 1500, 1462, 1437, 1358, 1286, 1122, 1090, 1041, 731, 619 cm⁻¹. **1b**: ¹H NMR (DMSO-*d*₆) δ 1.23~1.26 (m, 2H, -CH₂-),

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1.46~1.51 (m, 2H, $-\text{CH}_2-$), 1.65~1.71 (m, 2H, $-\text{CH}_2-$), 3.30 (t, 2H, $J=6.6$, $>\text{N}-[\text{CH}_2]_4-\text{CH}_2-\text{O}-$), 3.35~3.37 (m, 8H, $\equiv\text{C}-\text{CH}_2-\text{O}-$), 3.84 (t, 2H, $J=6.9$, 7.3, $>\text{N}-\text{CH}_2-[\text{CH}_2]_4-\text{O}-$), 4.15~4.19 (m, 3H, OH), 5.95 (t, 2H, $J=2.0$, 2.3, $\text{PyH}_{3,4}$), 6.71 (t, 2H, $J=2.0$, 2.3, $\text{PyH}_{2,5}$); IR (neat) ν 3378, 2937, 2870, 1500, 1463, 1438, 1373, 1282, 1117, 1092, 1043, 727, 619 cm^{-1} .

The formation of films **2a** and **2b** by electro-polymerization on a glassy carbon electrode, the electro-incorporation of palladium, and the evaluation of catalytic activities for the film electrodes were carried out in a similar manner to our previous paper²⁾.

3 RESULTS AND DISCUSSION

Figure 1 shows cyclic voltammograms observed during repetitive potential scans between 0 and 1.1 V vs. SCE in an electrolytic medium, 0.1M (mol dm^{-3}) Bu_4NBF_4 -acetonitrile containing 10 mM monomers **1a** and **1b**. Repetitive cycling leads to an intensification of the redox peaks, indicating that electrochemical polymerization of the monomers takes place on a glassy carbon disk electrode (Diameter = 3 mm, Surface area = 0.071 cm^2). The resulting films **2a** and **2b** adhered strongly to the glassy carbon disk electrode surface. The redox peak height of **1a** was lower compared with those of **1b**. This behavior can probably be accounted for by assuming that the rate of the polymerization at 2 and 5 position of pyrrole ring was suppressed by the steric hindrance of trihydroxyl alkane having short carbon chain.

The incorporation of palladium in the film electrodes **2a** and **2b**, which were prepared by the controlled-potential electrolysis (1.30 V vs. SCE), was performed by the immersion of the films in an aq. 50 mM Na_2PdCl_4 solution and the following electroreduction (-0.3 V) of permeated PdCl_4^{2-} ion in the films. The amount of incorporated palladium (W_{Pd}) was calculated on the basis of electricity passed during the two electron reduction of PdCl_4^{2-} to Pd^0 . The amount of incorporated palladium in **2a** and **2b**, which were formed under the polymerization electricity $Q_f = 0.14 \text{ C cm}^{-2}$, were 5.5 and 8.5 $\mu\text{g cm}^{-2}$, respectively. The quantity of palladium in **2a** was much less than those in **2b**. This fact suggests

that the permeation of PdCl_4^{2-} in matrix is reduced by a smaller space of **2a**. The amount of incorporated palladium in **2b** having five carbon chain was less than those of P5HPy ($Q_f = 0.14 \text{ C cm}^{-2}$, $W_{\text{Pd}} = 9.3 \mu\text{g cm}^{-2}$)²⁾.

Fig. 1 Cyclic voltammograms of **1a** (a) and **1b** (b) in an acetonitrile containing 0.1 M Bu_4NBF_4 on a glassy carbon disk electrode. Monomer concentration: 10 mM. Scan rate: 100 mV s^{-1} .

Fig. 2 Cathodic current-potential curves for the hydrogen evolution reaction on the palladium incorporated electrodes in a 50% ethanol-HCl buffer solution (pH=1): curve a, **2a** ($W_{\text{Pd}} = 5.5 \mu\text{g cm}^{-2}$); curve b, **2b** (8.5); curve c, P5HPy (9.3). $Q_f = 0.14 \text{ C cm}^{-2}$. Scan rate: 100 mV s^{-1} .

As shown in Fig. 2, when the current-potential curves for the palladium incorporated film electrodes **2a** and **2b** in an ethanol aqueous solution were measured, cathodic currents based on hydrogen evolution were observed. The film electrode **2a** and **2b** gave large current at *ca.* -0.2 and -0.3 V, respectively. In particular, the **2a** is a good catalytic electrode because the hydrogen evolution current increases at lower potential in spite of small amounts of palladium (Fig. 2, curve a). However, a clear explanation to the behavior of the film electrode **2a** could not be made. The cathodic current for the film electrode **2a** and **2b** increases linearly, while for P5HPy electrode containing much amount of palladium ($W_{Pd} = 9.3 \mu\text{g cm}^{-2}$), the suppression of current was observed in the latter half of potential sweep (Fig. 2, curve c). These results suggest that the migration of proton to palladium surface is enhanced by introduction of many hydroxyl groups in matrix.

For the film electrode **2b** a constant current for hydrogen evolution was observed over 100 hours at -0.4 V in an ethanol aqueous solution and the large current density was maintained at *ca.*

0.15 mA cm⁻². This stability is probably due to strong interaction of hydroxyl group with the glassy carbon electrode surface. Further studies to find out optimum condition for the system of electrocatalytic hydrogenation using these film electrodes are now in progress.

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