Chemistry Letters Vol.33, No.5 (2004)

Electrochemical Synthesis of Polypyrrole and Polythiophene in Supercritical Trifluoromethane

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(Received January 22, 2004; CL-040088)

Supercritical trifluoromethane (scCHF$_3$) has been used as an electrolytic medium for the electrooxidative polymerization of pyrrole and thiophene; both monomers could be electropolymerized apparently faster in scCHF$_3$ than in the coventional organic media like an acetonitrile solution, and the obtained films had highly-regulated structure.

Supercritical fluids such as super critical carbon dioxide (scCO$_2$) are becoming widely recognized as useful media for organic and polymer syntheses because of low toxicity, ease of solvent removal, potential for recycling, and variation of reaction rates by relatively small changes in pressure and temperature.[1–4] However, scCO$_2$ is unsuitable for electrochemical syntheses since it is highly nonpolar and low in solubilizing ability for supporting electrolytes, although the polarity and solubilizing ability are increased to some extent by the addition of a small amount of water or polar organic solvents.[5,6] Very recently, Mabrouk and co-workers reported the electrochemical synthesis of polypyrrole in scCO$_2$ containing 0.16 M pyrrole, 0.16 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$), and 13.1 vol % acetonitrile.[7]

Hence, supercritical fluoroform (scCHF$_3$) exhibits relatively high solubilizing ability and its dielectric constant can be controlled from 1 to 7 by manipulating either the temperature or the pressure of scCHF$_3$ without any additives like polar solvents.[8–10] Therefore, scCHF$_3$ is expected to be a better medium for electrochemical syntheses. In this paper, we describe the electrochemical synthesis of polypyrrole and polythiophene in scCHF$_3$. As far as we are aware, this is the first example of the electrochemical synthesis in scCHF$_3$.

Unless stated otherwise, the electrochemical synthesis of polypyrrole and polythiophene was carried out as follows.

In a stainless steel cell (Taiatsu Techno, Co., Tokyo, volume: 96 mL) equipped with Pt plates ($1 \times 1\,\mathrm{cm}^2$) as an anode and a cathode, respectively, Ag wire as a quasi reference electrode, and sapphire window for the observation of the inside, each monomer (10 mM) and TBAPF$_6$ (40 mM) as a supporting electrolyte were added, then liquid CHF$_3$ was injected at 5–15 MPa from a LC pump (NP-D-321J, Nihon Seimitsu Kagaku Co., Tokyo) connected to a CHF$_3$ gas cylinder. The cell was heated to 50 °C to create a supercritical state. The electropolymerization of pyrrole and thiophene was carried out by a potential scanning method at 20 cycles in a range of -0.5–$+1.2$ V and 0.0–$+2.0$ V vs Ag quasi reference electrode, respectively, at 100 mV s^{-1}. The electropolymerization was also carried out in a conventional medium such as an acetonitrile solution containing 10 mM of each monomer and 40 mM TBAPF$_6$ at 50 °C by a potential scanning method under the same electrolytic conditions described above. The polymer films deposited on the anode were subjected to infrared reflection absorption spectroscopy and scanning electron microscopy (SEM), and their thickness was measured by a displacement meter. Electroconductivity of the films prepared in scCHF$_3$ could not be measured because of difficulty of peeling off a test piece from the anode substrate.

Figures 1a and 1b show cyclic voltammograms in the course of polymerization of pyrrole at 20 times of potential scanning in scCHF$_3$ at 15 MPa and in a conventional medium like an acetonitrile solution, respectively. Although their shapes seem to be almost similar to each other, the oxidation and reduction peak currents of the voltammogram in scCHF$_3$ are higher than those in the acetonitrile solution. This fact indicates that the polymerization rate is increased in scCHF$_3$. Furthermore, as indicated in Figures 1c and 1d, thiophene can be electropolymerized about 10 times faster in supercritical CHF$_3$ than in an acetonitrile solution. A supercritical fluid such as scCHF$_3$ exhibits larger diffusivility and lower viscosity compared to those of conventional liquids, since physical properties of supercritical fluids are intermediate between those of gases and liquids.[11] Therefore, the mass transfer of monomers to the anode surface and the radical–radical coupling of oligomers in the electropolymerization process might be favorably affected in scCHF$_3$.

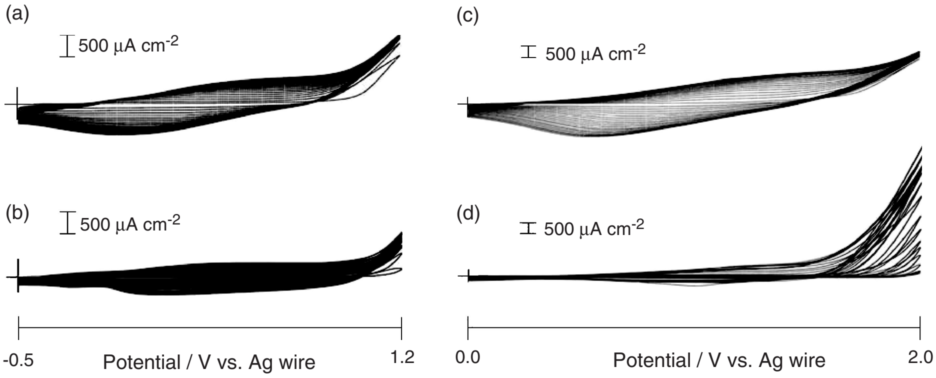

Figure 1. Cyclic voltammograms obtained during the course of polymerization of (a, b) pyrrole and (c, d) thiophene at 20 times of potential scanning in (a, c) scCHF$_3$ (15 MPa) and (b, d) acetonitrile solution.

Table 1. Properties of polypyrrole and polythiophene films prepared in acetonitrile solution and $scCHF_3$

Polymer	Media	Roughness Factor[a] / dimensionless	Average Thickness / μm	Electrochemical Capacity / C cm^{-3}
Polypyrrole	$scCHF_3$	0.03	0.4	150
Polypyrrole	CH_3CN	0.11	3.0	19
Polythiophene	$scCHF_3$	0.04	1.1	120
Polythiophene	CH_3CN	0.12	1.4	13

[a] Roughness factor is standard deviation of the film thickness.

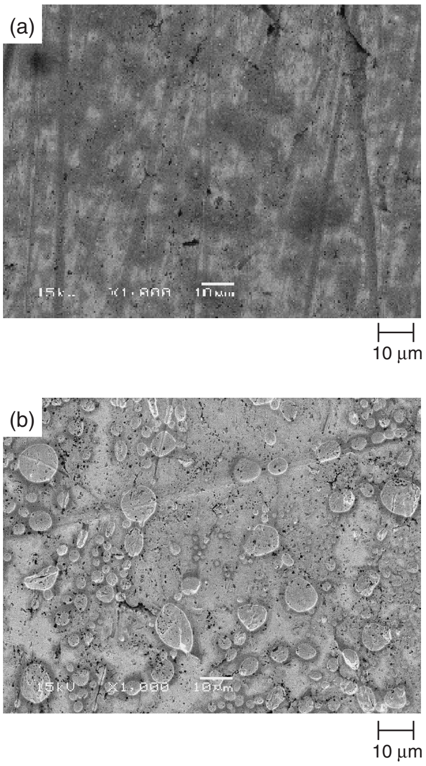

Figure 2. SEM photographs of polypyrrole films polymerized in (a) $scCHF_3$ and (b) acetonitrile solution.

Hence, below 13 MPa the polymerization rate in $scCHF_3$ decreased with precipitation of $TBAPF_6$ as a supporting electrolyte, and no polymerization current was observed below 10 MPa. This result accords exactly with the dependence of the dielectric constant of $scCHF_3$ on the applied pressure, since the constant decreased steeply below 10 MPa.[10] In addition, it is suggested that the polymerization rate can be controlled by manipulating the pressure of $scCHF_3$.

The IR spectra of both polymer films prepared in $scCHF_3$ were reflecting the α–α' conjugated polymer structure and identical completely to those of the electrochemically prepared in the conventional media reported elsewhere.[12,13]

On the other hand, the surface morphology of both polymer films deposited on the anode was observed by SEM. A porous structure with grains is observed in polypyrrole film polymerized in the acetonitrile solution as shown in Figure 2. In sharp contrast, the surface of the film prepared in $scCHF_3$ is so smooth that no grains could be observed even at high magnification. Similar trend could be also observed in SEM photographs of polythiophene films.

It is noted that some physical properties of the polypyrrole and polythiophene films are also greatly affected by the use of $scCHF_3$ as an electrolytic medium as summerized in Table 1. The films polymerized in $scCHF_3$ were thinner than those in the acetonitrile solution. However, an electrochemical capacity of the former films is higher than that of the latter films. Therefore, the films prepared in $scCHF_3$ are expected to be useful as a material for high-performance electrochemical capacitors.

In conclusion, pyrrole and thiophene can be electropolymerized apparently faster in supercritical CHF_3 than in the coventional organic media like an acetonitrile solution. The polymerization could be switched on and off by adjusting the pressure of $scCHF_3$. Furthermore, it is also found that conducting polymer films polymerized in $scCHF_3$ have highly-regulated structure. CHF_3 is not included in ozone-depletion fluorocarbons and can be used practically by recovering and recycling. Therefore, we believe that the application of $scCHF_3$ to electrochemical syntheses will become a new process not only for effective production but also for enviromentally-friendly production.

Further investigations of mechanistic aspects and for application to other monomers are currently in progress.

This study was financially supported by a Grant-in-Aid for Scientific Research from The Japanese Ministry of Education, Culture, Sports, Science and Technology.

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