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Electrochemical Synthesis and Characterization of Conducting Polymers in Supercritical Carbon Dioxide

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Received April 10, 2002

We wish to report the first successful electrochemical synthesis of conducting polymers (CPs), specifically, polypyrrole (PPy) and polyaniline (PAn), in supercritical carbon dioxide ($scCO_2$). Supercritical fluids (SCFs), such as supercritical CO_2, are practical green alternatives to the harsh and environmentally hazardous solvents traditionally used in conducting polymer synthesis such as sulfuric acid or acetonitrile.[1] The conducting polymers synthesized in $scCO_2$ were characterized with cyclic voltammetry (CV), four-point probe conductivity, scanning electron microscopy (SEM), and UV−vis spectroscopy. Preliminary data suggest that $scCO_2$-synthesized polypyrrole exhibits uniquely different morphological properties and high conductivity compared to those of polypyrrole synthesized electrochemically in aqueous and nonaqueous media.

CPs have recently been chemically synthesized in supercritical fluids.[2] Electrochemistry in supercritical fluids to date has been restricted to the study of simple redox systems such as ferrocene.[3−6] The present study is the first using $scCO_2$ as a solvent in electrochemical synthesis. PPy and PAn have recently received much attention for their use as corrosion inhibitors,[7,8] free-standing conductive membranes,[9,10] and in microelectronic devices.[11,12] Their electrochemical synthesis is well documented.[13−22]

The CPs were synthesized by repeated potential cycling of 0.16 M pyrrole in $scCO_2$ at ca. 2 mm × 5 mm rectangular indium tin oxide (ITO) glass electrodes (Delta Technologies, $R_s = 4-8\ \Omega$) in a 4.5 cm^3 stainless steel cell (see Supporting Information). The $scCO_2$ contained 0.011 mol of acetonitrile as modifier and 7.2×10^{-4} mol of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte. The cell itself served as both counter and reference electrode.[23] Figure 1 shows a representative CV for the electropolymerization of 0.16 M pyrrole in $scCO_2$ at 100 mV/s. Figure 2 shows the voltammogram obtained after the PPy-coated ITO electrode was removed from cell, rinsed with acetone, methanol, and deionized water, and placed in a 1 M H_2SO_4 solution. The appearance of the CV is comparable to that of PPy/ITO films prepared electrochemically in aqueous solution.[17,18] PAn has also been successfully electrochemically synthesized in $scCO_2$. Figure 3 shows the characteristic signature for a PAn/ITO electrode, which has been removed from the supercritical fluid cell, rinsed with acetone, methanol, and deionized water, and placed in a 1 M HCl/1 M NaCl[13−15] solution.

Four-point probe conductivity measurements (Lucas Signatone S-301-4) of $scCO_2$-synthesized PPy yielded a conductivity of 4.4 ± 2.0 S/cm ($n = 16$). The conductivity is comparable to that of PPy electrochemically synthesized in nonaqueous and aqueous media.[22]

Figure 4 shows scanning electron micrographs (JEOL JSM 3220) for PPy/ITO films synthesized in $scCO_2$ and acetonitrile. The $scCO_2$-synthesized PPy exhibits a markedly different surface morphology consisting of small, raised granular PPy nodules (0.5−3.0 μm) on a flat, continuous PPy surface (0.167 ± 0.08 μm, average thickness, $n = 10$). This is in contrast to the characteristic wrinkled texture of PPy typically observed in films synthesized in nonaqueous solutions.[22,24] The morphological characteristics exhibited by SCF-synthesized PPy may be advantageous in anticorrosion,[25] dielectric,[26] and optical applications.[27]

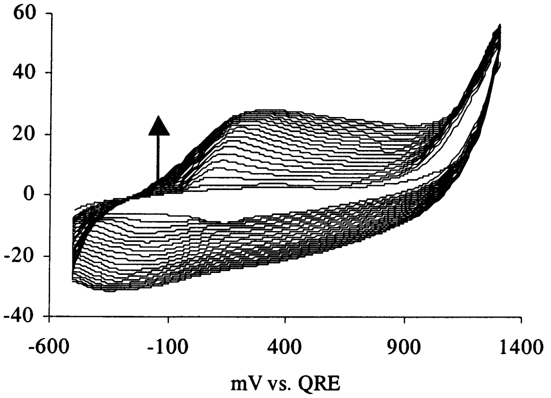

Figure 1. First 40 scans in the electropolymerization of pyrrole at ITO in $scCO_2$. Conditions: 1400 psi, 50 °C, 0.16 M pyrrole/0.16 M $TBAPF_6$/13.1 vol % acetonitrile, scan rate 100 mV/s. Arrow denotes increase of current upon successive scans.

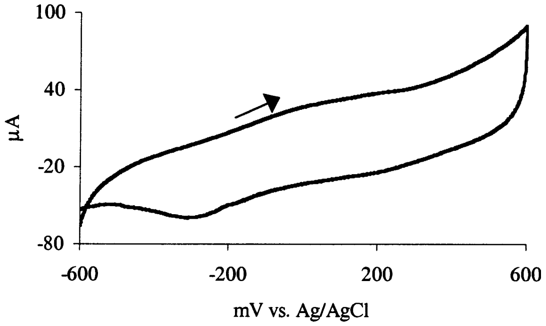

Figure 2. CV of $scCO_2$ synthesized polypyrrole/ITO in 1 M H_2SO_4. Conditions: PPy-coated ITO working electrode, platinum mesh counter electrode, Ag/AgCl (3 M NaCl) reference, scan rate 100 mV/s. Arrow indicates direction of scan.

Additional evidence for the successful synthesis of PPy and PAn in $scCO_2$ was provided by UV−vis spectroscopy. The UV−vis spectra for $scCO_2$-synthesized PPy/ITO and PAn/ITO films exhibited the characteristic polaron transitions at 425[20,28] and 450 nm,[28−30] respectively.

In summary, we have shown that electrochemical polymerization in $scCO_2$ is a viable alternative approach for the synthesis of

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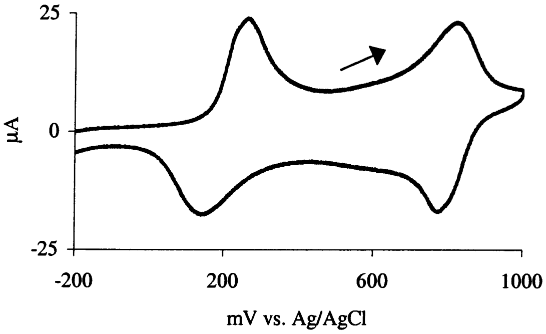

Figure 3. CV of scCO$_2$-synthesized PAn/ITO in a 1 M HCl/1 M NaCl solution; platinum mesh counter electrode, and Ag/AgCl (3 M NaCl) reference electrode, 100 mV/s. Conditions of PAn synthesis: 1170 psi, 40 °C, 0.16 M aniline hydrochloride/0.16 M TBAPF$_6$/13.1 vol % acetonitrile, scan rate 100 mV/s. Arrow indicates direction of scan.

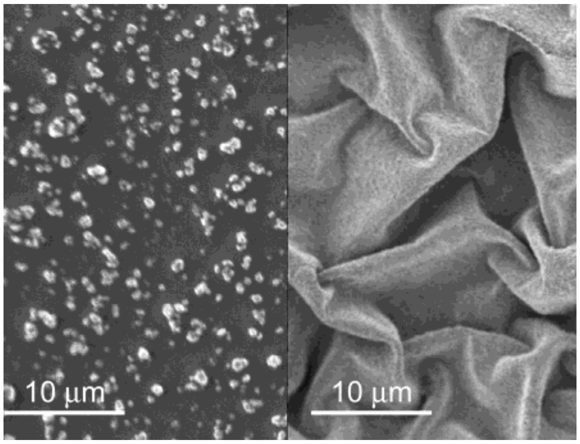

Figure 4. Scanning electron micrograph of PPy grown on ITO in scCO$_2$ using the experimental conditions of Figure 1, (left) and in 0.1 pyrrole/1 M TBAPF$_6$/acetonitrile (right). The scale is the same for both micrographs. The accelerating voltage was 1 keV. The average thickness for scCO$_2$-synthesized PPy is 0.167 ± 0.08 μm ($n = 10$) and 6.65 ± 0.3 μm ($n = 4$) for PPy synthesized in acetonitrile.

conducting polymeric materials. The conductivity of CPs synthesized in scCO$_2$ is comparable to that of CPs produced using the established synthetic routes for these polymers.[21,22,25] The films produced in scCO$_2$ in this study were visibly smoother and flatter and exhibited distinctive surface characteristics that could prove advantageous in optical,[27] dielectric,[26] and anticorrosion applications.[25] Efforts are currently in progress to optimize the electrochemical synthesis of CPs in SCFs and more thoroughly characterize the polymers produced, in view of their unique surface properties and the conductivities reported herein.

Acknowledgment. We thank the Department of Physics at Northeastern University, Dr. Timothy Swager, and Dr. Debra Mascaro of the Department of Chemistry at Massachusetts Institute of Technology (MIT) for the use of the four-point probe instrumentation. Microscopy was performed at the MIT Center for Materials Science and Engineering Electron Microscopy Facility. The work was supported by ACS PRF award 34546-AC4 and a Northeastern University RSDF Award to P.A.M.

Supporting Information Available: Experimental details pertaining to the electrochemical synthesis and characterization (PDF). This material is available free of charge at http://pubs.acs.org.

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JA026494C