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Effect of reactor configuration and temperature on Electropolymerization of Sodium Camphorsulfonate-Doped Polypyrrole

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Abstract. Real-time electrolyte pH profile during electropolymerization experiments were obtained for a single-compartment reactor (SCR) and a three-compartment reactor (3CR). The reaction products, polypyrroles doped with 10-camphorsulfonic acid sodium salt (CSS), were studied for electrical conductivity, texture, surface morphology and thermal gravimetric analysis (TGA). Results show progressive lowering of electrolyte pH values at the anode for the 3CR system. The pH values in the SCR remained relatively steady. Polypyrroles prepared using the 3CR system showed higher electrical conductivities and smoother surfaces than their SCR equivalents.

Abstrak. Plot pH terhadap masa semasa eksperimen elektropolimeran diperolehi untuk sel satu ruang (SCR) dan sel tiga ruang (3CR). Hasil tindakbalas, polipirol yang didop dengan garam natrium asid 10-kamfor sulfonik, dikaji sifat kekonduksian elektrik, tekstur, morfologi permukaan dan analisis gravimetri terma. Hasil kajian menunjukkan pengurangan secara progresif nilai pH pada anod untuk sistem 3CR. Nilai pH dalam sistem SCR kekal tetap. Polipirol yang disediakan dengan sistem 3CR menunjukkan kekonduksian elektrik yang tinggi dan permukaan yang rata berbanding dengan sistem SCR.

Key words: conducting polymer, electropolymerization, polypyrrole, reactor configuration.

Introduction

Conducting polymer suited for tailored applications in batteries, electronic displays, ion-selective electrodes, molecular transistors and molecular circuit elements have been the focus of many researches in the past two decades. Studies have been carried out on the role of a variety of processing parameters, such as temperature [1], solvent [2], monomer and dopant type, shape and size [3], static and pulse potential modes [4], on a number of polymer systems. The effect of *ex situ* acidic and basic electrolyte solution on the redox processes of polypyrrole (PPy) have been studied [5]. We report here the *in situ* electrolyte pH profiles during electropolymerization and the effect of reactor configuration and temperature on the conductivity, texture and morphology of Sodium camphorsulfonate-doped polypyrrole, PPy(CS).

Experimental

The pyrrole monomer (Aldrich) was distilled twice under reduced pressure and stored cold in the dark. Thin films of Sodium camphorsulfonate-dopped polypyrrole, PPy(SC) were prepared electrochemically using the Potentiostat/ Galvanostat 173 (Princeton Applied Research). The films were grown on a conductive indium-titanium oxide coating (ITO) on glass (Baltracon Z10) as the working electrode, with a carbon rod as the counter electrode. The anodic voltage was measured against a saturated calomel electrode (SCE). Solution pH was measured with a pH probe connected to a Conning Ion Analyzer 250. The pH , the working and counter potentials were interfaced to a LabVIEW virtual instrumentation program (National Instruments) on a laptop for real-time data collection, analysis and storage. Single-compartment (SCR) and three-compartment (3CR) electrochemical reactors of 100 ml capacities (Figure 1) were used.

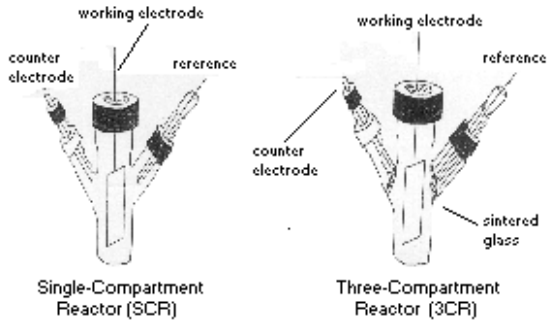

Figure 1: Single- and Three-Compartment Reactors

Aqueous solutions (deionised water) containing 0.2 mol l^{-1} of pyrrole and 0.1 mol l^{-1} of sodium camphorsulfonate (Aldrich) were electrolysed, with continuous stirring, at desired temperatures under

constant voltage 1.2 V (versus SCE) for a fixed time of 5 hours. The films were washed with deionised water and dried in a vacuum oven. The electrical conductivity of the films were measured using the four-pre technique. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA 7/Dx system and the Scanning electron microscopy was performed on a JEOL JSM-6400 microscope.

Results and Discussion

Typical pH profiles during electropolymerization in SCR and 3CR rectors is given in Figure 2. The results show that the extent of lowering in pH values, at any given temperature, is greater in 3CR.

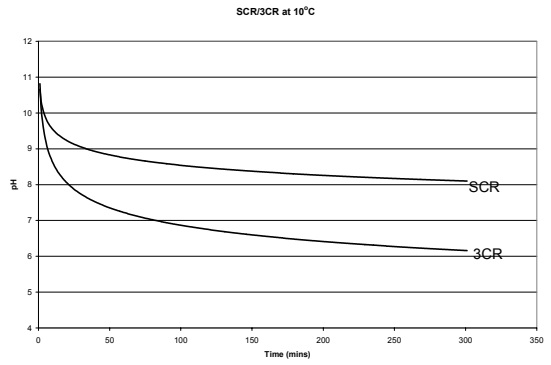

Figure 2: pH Profiles of the Electrolyte Solution During Electropolymerization of PPy(CS) in SCR and 3CR.

Similarly, the electrical conductivities of the corresponding PPy(CS) show improved values relative to those prepared using SCR reactors. This observation lean support to the theory that intercalation of counter ion (i.e. the CS anions) into the polymer should lead to lower pH. Electrical conductivity of the PPy films increased with decreasing temperature (Table 1). Similarly, SEM results show the average size of the polymer globules or clusters increased with low temperature. This shows there is a direct and significant link between molecular organization and the nature of charge transport. It has been suggested that the film is composed of highly disordered layered structure, in which the sheets of PPy chains are separated by layers of counter-ion units. Conduction may therefore be dominated by transport within individual sheets of polypyrrole, essentially a 2D hopping process. However, more information on the average molecular weight, length and distribution of polymer chains will be needed to fully understand the relationship between molecular ordering, super-molecular structure and charge transport.

Results from TGA are very similar for all the products, with weight losses at about 310ºC, 440ºC and 520ºC. Undopped PPy and SC gave weight loss at 254.5ºC and 379.9ºC respectively. The shift of the PPy and the SC thermograph to 310ºC and 440ºC could be due to weak electrostatic and weak intermolecular bonding.

Table 1: Summary of Results from SEM, Conductivity and TGA of PPy(CS) prepared in SCR and 3CR at different Temperatures.

	SCR			3CR	
	25 ºC	10 ºC	4 ºC	25 ºC	10 ºC
σ(Scm^{-1})	0.017	0.094	2.347	0.071	.0368
TGA (ºC)	310.0 441.3 520.7	314.1 445.0 520.2	309.0 441.7 521.4	313.7 440.7 525.6	314.6 444.1 522.0
SEM Size Texture Surface	 4-8µm compact rough++	 5-11µm porous rough++	 8-20µm porous++ smooth	 4-8µm porous+ smooth	 2-4µm porous rough

Conclution

These experiments have shown that the 3-compatment reactor yields better conducting PPy(CS) relative to the SCR at any given temperature. However, temperature is a more critical parameter in determining conductivity and morphology of PPy(SC) films than the configuration of the electrochemical reactor cell. Low temperature generally enhanced electrical conductance and smoothness of the PPy(CS) films.

Acknowledgement

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