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Deposition and characterization of functional coatings based on PDPA/Ag nanostructured materials

1. Introduction

Organic semiconducting materials receiving a constantly growing attention owing to a valuable combination of properties making them excellent basis for functional coatings for a wide range of applications. Of particular interest are hybrid nanostructured materials based on conducting polymers that may be tuned to meet the requirements for organic printable and wearable electronics, electrochemical and optical sensors as well as energy harvesting, storage and conversion devices. Among the key features of poly(diphenylamine) (PDPA) as promising basis for functional nanocomposites are high redox-reactivity, switchable conductivity and electrochromic properties. The processes of in situ formation of nanocomposites based on poly(diphenylamine) as a result of oxidative polymerization with Ag/Fe bimetallic system for obtaining smart functional coatings have been investigated.

3. Controlled formation approaches

Basic approaches

- **Two-step**

  The nanoparticles are synthesized preliminary and embedded into polymeric matrices

- **Single-step**

  The formation of nanoparticles and polimerization occurs at the same time

- **Control possibilities**

  Concentration and concentration ratio, temperature, mixing, modification and stabilization additives

Dynamic approaches

- **Frequency control**

  The nanocomposite formation process includes series of discrete pulses of polarization with programmed shape and frequency

- **Electrochromic coupling**

  Polarization pulses may be applied conditionally based on changes in optical properties of the sample

- **Control possibilities**

  All traditional + software-defined conditional application of precise polarization pulses and bias.

4. Hardware architecture

Advanced Reaction Controller

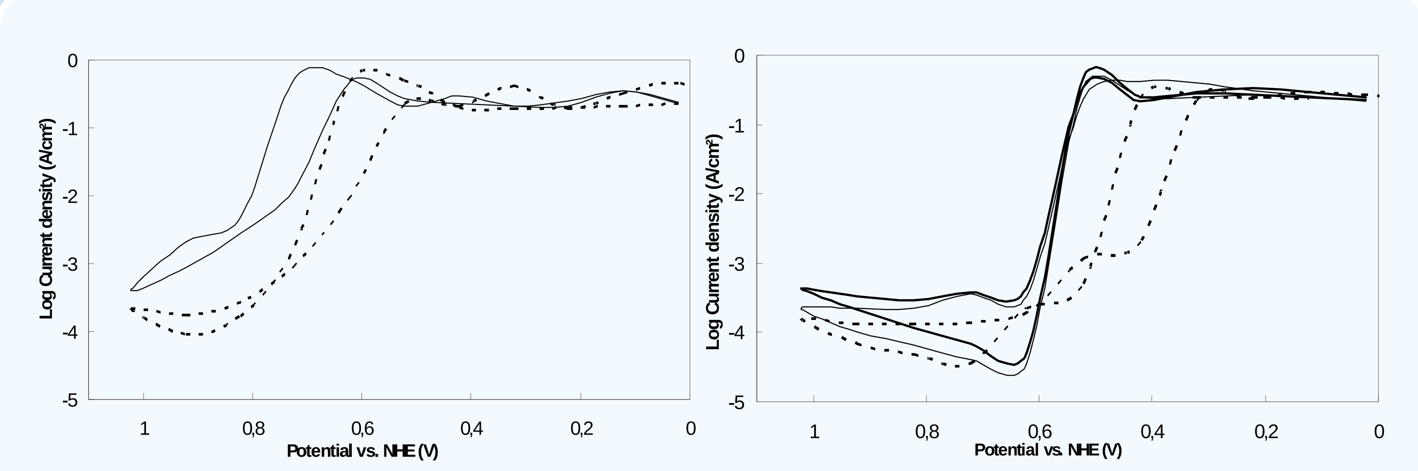
- **Application controller** — High-performance CPU
- **Potentiostat** — 16-bit ADC
- **Controller**
- FPGA-based universal programmable real time processing unit

Universal chamber

- Reaction cell
- Optical system
- Thermal control
- pH meter
- Steering

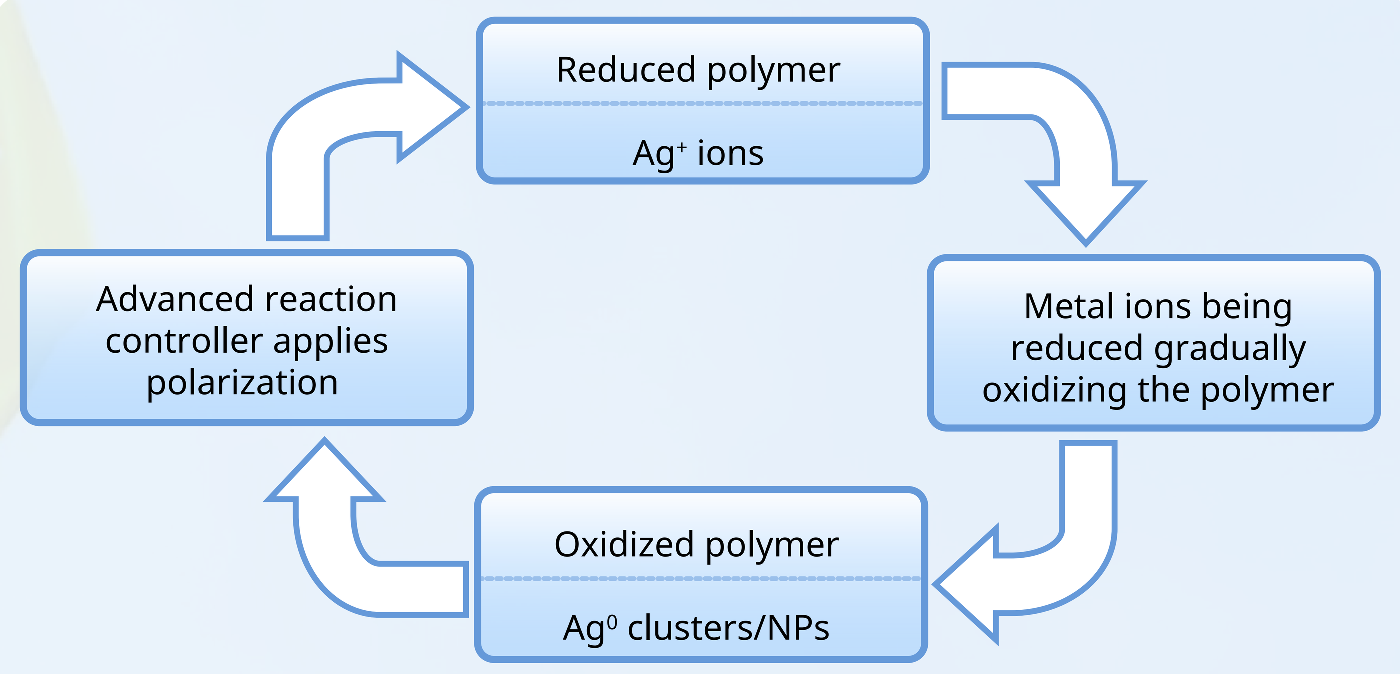
2. Experimental results

In contrast to plain $DPA/AgNO_3$ pair, introduction of Fe^{2+}/Fe^{3+} ions redox system delivers additional route for oxidative polymerization of DPA monomers without formation of Fe NPs. Electrochemical behavior has been studied using linear sweep cyclic voltammetry. Sharp decrease in a current density at 0.65V that is attributed to a process of switching the polymer to a non-conductive state may be observed on both forward and reverse polarization scans.



Cyclic Voltammograms of the PDPA a) and PDPA/Ag b) on the steel support plate within a potential window of 0 to 1.0 V versus NHE. Scan rate is 10 mV/s

Electrochromic behavior is found to be similar to the undoped PDPA film. After switching off the polarization, the formed PDPA relaxing rapidly from colored to a fully transparent state. Obtained hybrid coatings have been characterized using SEM, AFM, FTIR, Raman and Auger spectroscopy methods. It was discovered that silver nanoparticles are found to be uniformly dispersed in polymeric matrices and mostly spherically shaped with sizes in range 40-50 nm.



Thus, PDPA/Ag nanocomposites may be prepared via single step synthesis in bimatallic Ag/Fe system. Poly(diphenylamine) retains switchable conductivity and electrochromic properties within a composite and may be reversibly oxidized or reduced under different polarization and pH conditions making it excellent basis for chemoresistor- and transistor-type sensing devices.

5. Data processing and analysis

Schematic diagram

Automated monitoring and control module — Controls operation via scripts and collects experimental data

- **Potentiostatic system**
- **FPGA control**
- **Optical spectrum analyzer**
- **Hi-precision pH-meter**

Reaction chamber — Contains polymeric film + metal-containing precursor

Reaction controller capabilities

Monitoring

- Electrochemical parameters
- Spectral parameters
- pH & temperature

Artificial neural network data analysis

- Aggregation & prediction
- Geometrical and structural parameters
- End-product reactivity

Control

- Polarization potential
- Activation threshold
- Frequency limit
- Adaptive AI control