ELECTROSYNTHESIS OF PANI-POWDER USING ANODIZED ALUMINUM

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Introduction

It is now usual practice to deposit polyaniline (PAni) from aqueous acid solutions. Substrates were preferentially inert materials as platinum, gold and glassy carbon. Since 1988, it is being deposited polymers on active metals as iron and aluminum [1]. For electropolymerization of PAni, a potential window between -0.2 and +0.8 V vs. SCE is used. At this potential range, the most active metals dissolve anodically forming passive films, which is a real competition to the formation of the polymer.

Chemical synthesis of PAni using oxidants, brings a problem related with their recycling, along with the contamination of the product. Battery quality polymers can be prepared by electrodeposition of polymer powders.

Similar to the preparation of polypyrrol powder proposed by Hulser et al., we report here about the electrosynthesis of powdery PAni on previously anodized aluminum. To avoid overoxidation we propose the galvanostatic deposition, thereby the potential is controlled by fixing the applied current density.

Experimental

Aluminum disk of 1 cm^2 surface area was used as electrode. An electrical connection lead of Pt wire was spot-welded on the backside of the Al disk. The sample was then embedded in acrylic resin leaving part of the wire free. After polishing in emery paper (320-1200 grade), degreasing in ethanol and drying at 40°C, the specimen was submitted to anodic activation in 0.1 M aniline + 0.1 M HNO_3. The activation was performed potentiodynamically at 2 mV s^{-1}. After anodic activation, the specimens were characterized by electrochemical impedance spectroscopy. A single compartment electrochemical cell, with a platinum foil (2 x 2 cm) counter electrode and a saturated calomel electrode (SCE) reference electrode, was used. Aniline was distilled over zinc dust to remove the oxidation impurities. The deposition electrolytes were: 0.4 M aniline in 0.5 M H_2SO_4 or 0.8 M aniline in 1 M HNO_3. All electrolytes were prepared by using Milli-Q water. The measuring equipment was a potentiostat/galvanostat 273 A (EG&G), connected to a frequency response analyzer FRA 1255 from Solartron for impedance measurements. The accumulated powder in the bottom of the cell was separated by filtration and washed with 1 M HCl solution. After filtration, the powder was dried under vacuum in an desiccator. It followed then de-doping in 0.1 M NH_4OH solution for 20 hours under agitation, to neutralize the acid in the polymer. After de-doping, the powder was filtered and dried again in an desiccator, and finally conserved in vacuum until analysis. PAni was characterized by UV-vis-Spectroscopy. For that, a 5% solution of de-doped PAni in N-methyl-pyrrolydinone (NMP) was prepared, and its spectra was measured. Thereafter, the sample was doped by droplets of 5 M HCl solution and the spectra of doped PAni was measured. For analysis by infrared spectroscopy, the powder was triturated with KBr and a tablet was pressed.

Results

As reported elsewhere [2], the objective of a potentiodynamic anodic activation of Al in 0.1 M HNO_3 with 0.1 M aniline was to form pits which are filled with PAni. Pits usually form on aluminum surface at the pitting potential of 1.78 V vs. SCE as indicated by a steep current rise. By examining the surface after the first activation in 0.1 M HNO_3 with 0.1 M aniline, a very few amount of pits was observed on the anodized surface. Four more anodizations produced a great amount of pits filled with PAni. The prepared surface with the sufficient amounts of pits was then used as precipitation electrode. PAni powder obtained galvanostatically at 1 - 4 mA cm^{-2} from both solutions, 0.4 M aniline in 0.5 H_2SO_4 and 0.8 M aniline in 1 M HNO_3, are similar in size. It should be noted that 1 M HNO_3 with 0.8 M aniline solution turns red with increasing the quantity of galvanostatic depositions. However, the deposition electrolyte of 0.5 M H_2SO_4 with 0.4 M aniline does not change in color. Color changes of HNO_3 solution is attributed to the formation of soluble aniline oligomer in the electrolyte. The impedance spectra of the potentiodynamically activated surfaces in monomer-free and monomer-containing 0.1 M HNO_3 were almost same. The powder production in nitric attains higher current efficiency than in sulfuric acid. A copious selves falling fine powder is observed within the red turning electrolyte. In sulfuric acid, by contrast, a green powder is formed.

The UV-vis-spectra of PAni powder produced in H_2SO_4 shows absorption bands at around 325 nm and 620 nm for the de-doped , and at 365 nm and 820 nm for the doped PAni. The infrared spectrum of the de-doped PAni shows the two characteristic bands at 1447 and 1401 cm^{-1} corresponding to quinone and benzoquinone, respectively. Other bands at 1304, 1099 and 797 cm^{-1} correspond to vibrations in plane of C-N in quinoides and benzoquinoides and vibrations out in plane of C-H, respectively. The benzoquinone peak is very high compared to the quinone peak indicating that the PAni belongs to the reduced state.

One could observe that after many galvanostatic depositions the PAni-filled pits are protruded by growing oxide during the course of depositions.

Pre-activated aluminum electrode can be destinated exclusively to the production of PAni powder for the polymer is hindered to grow as an uniform layer and, therefore, it falls as powder.

1. P. Hulser, F. Beck, J. Electrochem. Soc., 137, 2067 (1990).
2. D. Huerta-Vilca, S.R. de Moraes, A.J. Motheo, Synth. Metals, submitted.