Redox switching hysteresis in polyaniline-acetate systems: a search of molecular factors important for the dynamics of the polymer reaction.

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Rok wydania

2004

Czasopismo

Journal of Electroanalytical Chemistry

Numer woluminu

571

Strony

51-57

DOI

10.1016/j.jelechem.2004.04.012

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The CV redox hysteresis of three polyaniline–aqueous trihalogenoacetic acid systems has been analyzed. The polymer phases studied involve monocarboxylate monoanion bases characterized by similar pK_a values in water to narrow the differences in molecular interactions. The hysteresis diminishes by 70 mV with size of the anions – from trifluoroacetate, through trichloroacetate, to tribromoacetate. The diffusion coefficients of the trihalogenoacetate anions in the oxidized polyaniline do not differ significantly. Their values are of the order of 10^{-10} cm^2/s, which is one order of magnitude lower than for the chloride anion in polyaniline. Ex situ 1750–1050 cm^{-1} Raman spectra of polyaniline–trihalogenoacetates show small noticeable systematic changes that correlate with the hysteresis behavior. Electrochemical impedance spectroscopy provides evidence for the chemical rate process involved in the redox switching of the polyaniline–tribromoacetate system.

Słowa kluczowe

Polyaniline, Trihalogenoacetic acids, Redox hysteresis, Redox dynamics, Cyclic voltammetry, Electrochemical impedance spectroscopy, Raman spectroscopy

Adres publiczny

https://doi.org/10.1016/j.jelechem.2004.04.012

Strona internetowa wydawcy

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