

Kinetics of Redox Switching of Electroactive Polymers Using the Electrochemical Quartz Crystal Microbalance. II. Identifying the Rate Limiting Step for the Redox Switch of Poly(vinylferrocene) in Aqueous Sodium Hexafluorophosphate Solutions

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The electro oxidation of poly(vinylferrocene) (PVF) films in aqueous bathing solutions proceeds via the oxidation of the uncharged PVF that is accompanied by the entry of counter ion and water into the film. Either of these latter two steps may be kinetically controlled. The change in mechanism between rate controlling coupled electron/ion and solvent transfer was studied in 0.1 M sodium hexafluorophosphate bathing solution using the electrochemical quartz crystal microbalance (EQCM). The film's redox switching was investigated using cyclic voltammetry at voltage scan rates between 0.004 V s⁻¹ and 0.050 V s⁻¹ and potential steps between 0 V and 0.6 V (or 0.7 V). The controlling kinetic step depends on the instantaneous oxidation state of the film, the time-scale of the experiment (potential jump or voltage scan rate), the film's instantaneous water content and whether the film is undergoing oxidation or reduction. The flux ratio of water to counter ion (ρ) during the redox cycle was used to characterize the rate controlling processes.

Our results show that during redox switching the counter ion content (redox state) and solvent content (solvation state) can be temporally decoupled and unrepresentative of the equilibrium situation, even under typical voltammetric conditions. (See Figure 1, Panels A and B This is particularly apparent in potential step experiments in which the time scale is shorter. Anomalous ρ_q - values occur at relatively low charge levels during both oxidation and reduction of PVF. The current and charge density dependences of ρ_q , suggest the interconversion of partially oxidized PVF states having the same oxidation level, but different water contents. Estimates of the equilibrium ratio of water flux to counter ion flux, $\rho_{equil,q}$ obtained from cyclic voltammetric and potential jump data lie in the range 3 to 4.

The change of the mobile species populations in the film observed for complete redox conversion between fully reduced and fully oxidized state is not a reliable guide to film composition at intermediate film redox states. The latter depend on film history and electrochemical technique more so than for fully oxidized and reduced forms. This is not widely appreciated. In order to understand the behavior

over a wide range of charge levels and time scales, which can require using different electrochemical techniques.

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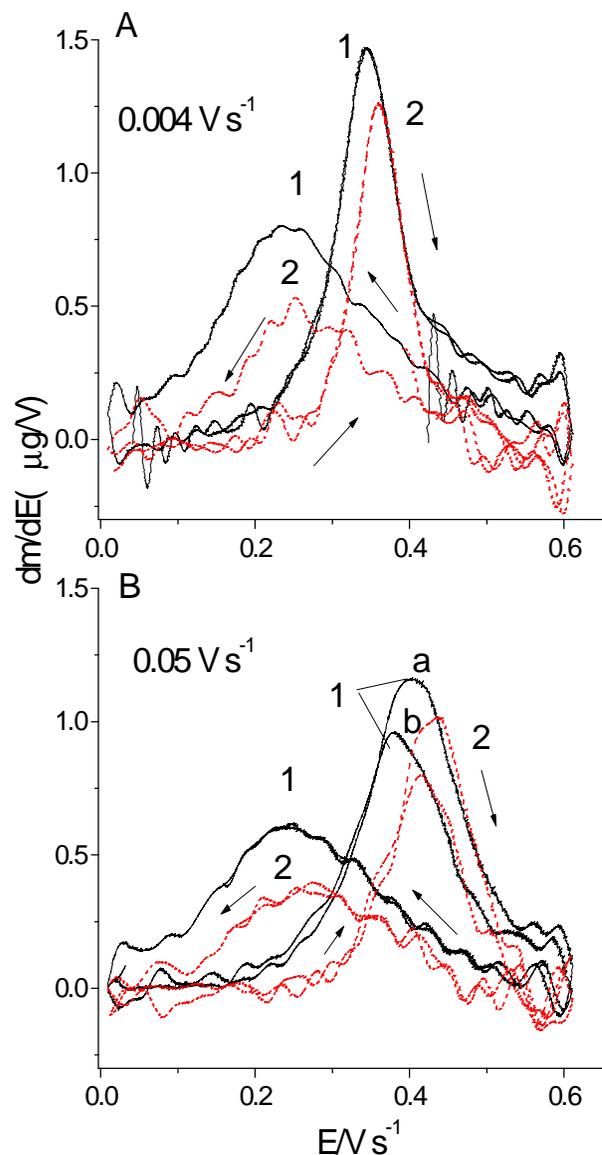


Figure 3. Rate of change of water (dotted curves) and PF_6^- masses (solid curves) with respect to potential vs potential for PVF in 0.1 M NaPF_6 . Panel A: $v_s = 0.004 \text{ V s}^{-1}$, Panel B: $v_s = 0.050 \text{ V s}^{-1}$. Data for two potential cycles are shown.

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of a polymer modified electrode, it is necessary to investigate it