

Abstract

From the defects-free self-assembled organic layers (SAMs) of $\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}$ molecules with short chain lengths ($n=4,6,8$) electrodeposited on the (111) surface of monocrystalline gold previously prepared, monitored defects (pinholes) were potential-induced from cyclic partial reduction of SAMs at an appropriate potential. Electrochemical impedance measurements were *in-situ* conducted and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ions were used as probes for mass and charge transfer. Interface evolution was modeled with an equivalent electrical circuit containing two distinct constant-phase elements (CPEs). One is a generalized semi-infinite Warburg element in series with a charge transfer resistance attributed to subdiffusion phenomenon through leaky sublayers at low frequencies; the other CPE is used for characterizing the interface heterogeneity at medium and high frequencies. At low frequencies, electrochemical impedance measurements show subdiffusion phenomenon, which depends on the remaining sublayer and its thickness. When the defect density increases, diffusion tends to be ordinary, obeying the Fick's law.