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Full Paper

Multiple Mechanisms for Electron Transfer at Metal/Self-Assembled Monolayer/Room-Temperature Ionic Liquid Junctions: Dynamical Arrest versus Frictional Control and Non-Adiabaticity

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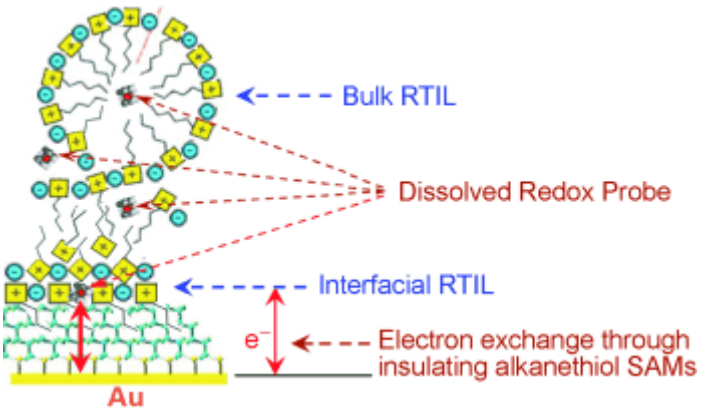
Abstract

When all the mechanisms go marching in: Electrochemical devices consisting of Au electrodes coated by self-assembled alkanethiol monolayers of variable thickness, a ferrocene/ferrocenium redox probe and [bmim][NTf_2] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) as the solvent (see picture), under variable overvoltage, temperature and pressure conditions, allowed the disclosure of three different electron-transfer patterns.



Electrochemical devices consisting of gold electrodes coated by electronically well-behaved self-assembled alkanethiol monolayers of variable thickness, a ferrocene/ferrocenium redox probe and a typical room-temperature ionic liquid (RTIL) [bmim][NTf_2] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) as a unique reaction medium with an exceptionally broad spectrum of relaxational modes (probed under variable temperature and pressure conditions), have been used to vary the intrinsic electron-transfer (ET) rate constant over eight orders of magnitude (from 0.1 to 3×10^{7} s^{-1}) by further tuning of the overvoltage. A remarkable interplay of ET mechanisms was observed, which was accompanied by the stepwise drop in the reorganisation free energy of the medium from 1.0 to 0.1 eV. The first mechanistic changeover to the dynamically arrested regime, with a locking ultra-slow relaxation time of approximately

50 μs, occurred at donor–acceptor separations below 20 Å. Another mechanistic changeover to the full solvent friction regime, controlled by a medium relaxation process of approximately 100 ns, emerged for ET distances smaller than 8 Å.

Supporting Information

Detailed facts of importance to specialist readers are published as ”Supporting Information”. Such documents are peer-reviewed, but not copy-edited or typeset. They are made available as submitted by the authors.

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