ELECTROCHEMICAL GENERATION OF SOLUTION-PHASE HOT ELECTRONS AT Ta/Ta_2O_5 & $Ta/Ta_2O_5/Pt$ ELECTRODES BY ELECTROCHEMILUMINESCENCE

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This paper deals with electrochemical processes involving hot electrons in the solution phase. Hot electrons are defined as electrons with thermal energies (kT_h) greater than the thermal energy (kT) of a phase[1] or as as electrons at an energy far above the Fermi energy of a phase[2]. Experimental evidence for the production of hot electrons (e_h^s) in an acetonitrile solution from a Ta_2O_5-covered Ta electrode was provided by electrochemiluminescence (ECL) and electrochemical measurements. Electron transfer to solution species occurred via the Ta_2O_5 conduction band, as demonstrated by comparative measurements with a number of one electron redox couples at Pt and Ta electrodes (Figure 1). The oxidized forms of thianthrene and a heptamethine cyanine dye were selected as the species capable of direct formation of the excited state and ECL upon hot electron injection. The observation of ECL emission upon a cathodic potential step (a process that does not occur at a metal electrode) confirmed the occurrence of this process (Figure 2). ECL emission at Ta/Ta_2O_5 was also observed during reduction of $Ru(bpy)_3^{3+}$ (bpy = bipyridine). Reasons for the low efficiency of the ECL process via hot electrons at the metal/metal oxide/solution interface are discussed. Rather thermalization of hot electrons via surface processes probably is the main cause inefficiency.

Interestingly, deposition of thin film of Pt on the Ta_2O_5 surface significantly enhanced the emission, as long as the Pt film thickness was below the mean free path of a hot electron in the Pt (e_h^{Pt}) (~50 –100 nm for a 3eV electron) (Figure 1 and 3). The enhancement of ECL efficiency at the metal/oxide/Pt/solution interface is ascribed to the suppression of the Ta_2O_5 surface states by the Pt film. In examining the $Ta/Ta_2O_5/Pt$/solution system, one can contrast the behavior observed when an electrical connection is made directly to the Pt with that observed when a connection to the Pt is made via the Ta, where e_h^{Pt} species are generated (Figure 4).

[1] Schmidt, W. F. *Liquid-State Electronics of Insulating Liquids*; CRC Press: Boca Raton, FL, 1997.
[2] Morrison, S. R. *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*; Plenum Press: New York, 1980.