CATHODIC ELECTROCHEMILUMINESCENCE OF $Ru(bpy)_3^{2+}$ CHELATE AT OXIDE-COATED SILICON ELECTRODES

Qinghong. Jiang[1], Johanna Suomi[1], Markus Håkansson[1], Antti J. Niskanen[2], Miia Kotiranta[1] and Sakari Kulmala[1,*]

[1]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, P.O. Box 6100,Fin-02015 HUT, Finland

[2]Microelectronics Center, Helsinki University of Technology, P.O. Box 3500, FIN-02015 HUT, Finland

Abstract

High-amplitude cathodic pulse-polarization of ultrathin oxide film-coated silicon electrodes induces tunnel emission of hot electrons into aqueous electrolyte solution which probably results in the generation of hydrated electrons in the vicinity of the electrode surface.

The method allows the detection of ruthenium (II) tris- (2,2'-bipyridine) chelate at subnanomolar concentration level. This paper shows that both n- and p- type heavily doped silicon electrodes can be used, illustrates the effect of oxide film thickness upon the silicon electrode on the intensity of ECL of ruthenium (II) tris- (2,2'-bipyridine) and discusses the basic features of ruthenium (II) tris- (2,2'-bipyridine) chelate-specific ECL at these electrodes.

Thin oxide film-coated silicon electrodes provide a lower blank emission and a higher ECL intensity of the present ruthenium chelate than oxide-covered aluminium electrodes[1]. This suggests that thin oxide film-coated silicon is a very promising working electrode material, especially in microanalytical systems made fully or partly of silicon.

The optimal oxide film thickness was around 2-6 nm (Fig. 1). Optimal pH was 9 and optimal consentration for peroxodisulfate ion which was used as a coreactant was ca. $3x10^{-2}$ M [Fig. 2]. Calibration plots for $Ru(bpy)_3^{2+}$ obtained in the optimal conditions are presented in Fig. 3. Luminescence lifetime of $Ru(bpy)_3^{2+}$ is so short that time-resolved detection provided much higher detetion limits than just recording the ECL intensity during the cathodic excitation pulse. Insett of Fig. 3 displays the uncorrected emission spectrum of the present label chelate.

The present ECL generation technique has a lot of potential for applications in miniaturized analysis, and in devices fabricated using highly sophisticated silicon technology of the present day, especially, for bioaffinity assays.

References

1. T. Ala-Kleme, S. Kulmala, L. Väre, M. Helin, Anal. Chem 71 (1999) 5538.

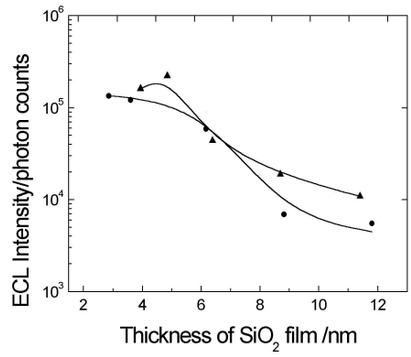

Fig. 1. Effect of oxide film thickness on ECL $Ru(bpy)_3^{2+}$. (●) n^+-Si and (▲) and p^+-Si. Conditions: 0.05 M $Na_2B_4O_7$ buffer at pH 9.2, 1.0×10^{-3} M $K_2S_4O_8$, 1.0×10^{-6} M $Ru(bpy)_3^{2+}$, pulse charge 480 μC, voltage -50 V, frequency 50 Hz,

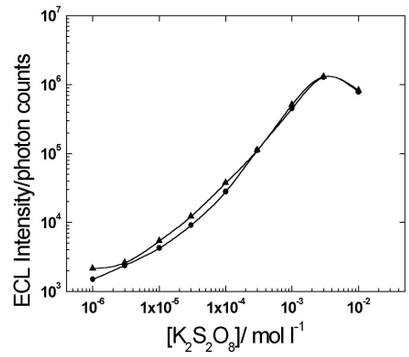

Fig. 2. Effect of $K_2S_2O_8$ concentration on $Ru(bpy)_3^{2+}$ chelate ECL. Conditions: 1.0×10^{-6} M $Ru(bpy)_3^{2+}$ in 0.05M $Na_2B_4O_7$ at pH9.2, coulostatic pulse generator, pulse charge 300μC, voltage -25V, frequency 50Hz , (●) n^+-Si (thickness of oxide film 3.6nm), (▲) and p^+-Si (thickness of oxide film 3.9 nm) as WE , respectively. ECL intensity was integrated over 1000 excitation cycles.

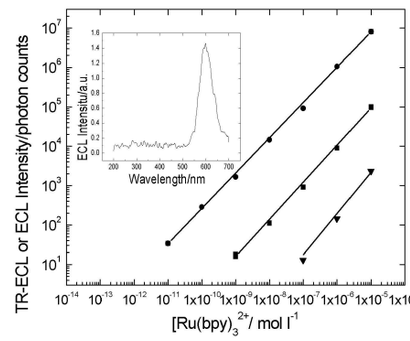

Fig. 3. Calibration curve for $Ru(bpy)_3^{2+}$ using disposable electrodes and either cathodic signal or time-resolved signal after the excitation pulse. (●) Cathodic ECL at disposable n-silicon electrodes with 3.6-nm thermal oxide film coating, (▼) Time-resolved signal at oxide-coated n-silicon electrodes (■) Time resolved signal using disposable oxide-covered aluminum electrodes. Conditions: 0.05M $Na_2B_4O_7$ buffer at pH 9.2, 3.0×10^{-3}M $K_2S_4O_8$, pulse charge 120 μC, pulse length ca. 560 μs,pulse voltage -45 V, pulse frequency 20Hz, Time-resolved measurements: delay time 0 μs, gate time 200 μs. ECL intensity was integrated over 1000 excitation cycles.