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# Quenching of cathodic electrogenerated F-center luminescence of aluminium oxide by lanthanide cations at the electrode/electrolyte interface

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## Abstract

Energy transfer between aluminium oxide F-center and lanthanide cations at an oxide-covered aluminium electrode during the cathodic pulse-polarization of the electrode is investigated by means of Stern-Volmer luminescence quenching kinetics. Terbium$^{III}$-specific extrinsic luminescence is observed while some other lanthanides are observed to quench the F-center luminescence. Different quenching efficiencies of the lanthanides are discussed to be dependent on the different energy acceptor characteristics of the tri- or divalent lanthanides.

*Keywords:* Cathodic luminescence; Luminescence quenching; Aluminium oxide F-center; Lanthanides

## 1. Introduction

Lanthanide$^{III}$ (Ln$^{III}$) chelates are well-known labelling compounds in bioaffinity assays. Their detection is based either on photoluminescence (PL) [1] or on cathodic electrogenerated luminescence (EL) at an oxide-covered aluminium electrode [2]. In the last-mentioned case the sensitivity of the detection of the luminescing label is dependent on the present background luminescence, i.e. the intrinsic cathodic luminescence of an oxide-covered aluminium electrode. Our recent studies show that F-center luminescence from an oxide-covered aluminium cathode is generated when a strong oxidant is presented in an aqueous electrolyte [3,4]. The mechanism of the luminescence is proposed to be associated with a two-step reduction of aqueous persulfate anion or hydrogen peroxide near the electrode/electrolyte interface. The mechanism is analogous to that previously presented for band gap luminescence of an n-type GaP semiconductor cathode [5]. Studies with GaP and other semiconductors have shown that in cases where both conduction band and valence band electrons participate in two-step reductions of, e.g. persulfate anion, hydrogen peroxide or benzoquinone, band gap luminescence of the semiconductor is observed. Both bands are participating in the reductions if the redox potentials (energy levels) of the two steps lie appropriately concerning the band distribution of the semiconductor.

Nowadays, it is known that there is a sub-band of F$^+$- and F-centers [6,7] (one or two electrons trapped on an oxygen ion vacancy) in the band structure of $Al_2O_3$ ca. 6.1 eV below the conduction band edge of $Al_2O_3$ which has been reported to lie at ca. −1.1 eV [8] (all values on the vacuum scale). Taking into account that the energy levels of the conduction band edge of water [9] and hydrated electron [10] have been reported to lie at ca. −1.3 eV and −1.5 eV, it can be stated that the electrons Fowler-Nordheim tunnelled to the conduction band of $Al_2O_3$ are able to occupy the level of the hydrated electron in the aqueous solution as well as the unrelaxed excited state ($^1$P state) of the F-center in $Al_2O_3$ which has been reported to lie very close, if not in the conduction band of $Al_2O_3$ [7]. The $^1$P state is nonradiatively relaxed to the $^3$P state at ca. −4.2 eV which is then radiatively relaxed to the $^1$S ground state of the F-center at ca. −7.2 eV. The proposed reaction scheme for the F-center luminescence involves an oxidation of the F-center by the sulfate radical formed from the persulfate anion via one-electron reduction by the hydrated electron.

$$e^- \rightarrow e^-_{aq} \tag{1a}$$

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} \tag{1b}$$

$$e^- \rightarrow F^+ \tag{2}$$

$$F^+ + e^- \rightarrow F^*(\vdash {}^1P) \tag{3}$$

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$$F^*(\vdash {}^1P) \rightarrow F^*(\vdash {}^3P) \tag{4}$$

$$F^*(\vdash {}^3P) \rightarrow F(\vdash {}^1S) + h\nu \tag{5}$$

$$SO_4^{\cdot -} + F \rightarrow F^+ + SO_4^{2-} \tag{6}$$

The oxidation of the F-center by the sulfate radical is favourable, taking into account that the energy level of the sulfate radical has been reported to lie at ca. −7.7 eV [11]. In the presence of hydrogen peroxide only a weak long-wavelength side tail of the F-center luminescence spectrum is observed [4]. This is understandable because the energy level of the hydroxyl radical formed from hydrogen peroxide via one-electron reduction by the hydrated electron has been reported to lie at ca. −6.6 eV at pH 9.2 [12].

In the present contribution, energy transfer between the F-center and lanthanide cations is investigated by means of Stern-Volmer luminescence quenching kinetics. Terbium$^{III}$-specific extrinsic luminescence is observed while some other lanthanides are observed to quench the F-center luminescence. Different quenching efficiencies of the lanthanides are discussed to be dependent on the different energy acceptor characteristics of the tri- or divalent lanthanides.

## 2. Experimental

### 2.1. Apparatus

Cathodic EL measurements were made by applying a ca. 60 V cathodic pulse to a cell which consists of an aluminium plate cathode (99.9%, E. Merck), a 0.2 mol l$^{-1}$ boric acid/borate buffered aqueous electrolyte, and a platinum wire anode. A 200 μC coulostatic (constant charge) pulse was used in the measurements with an 80 Hz frequency. The current in the cell was ca. 1 A during the pulse. EL spectra were scanned between 250 and 800 nm using the grating monochromator and the detector of a Perkin-Elmer LS-5 luminescence spectrometer with a scan speed 240 nm min$^{-1}$ and a 20 nm slit. EL decay curves were recorded using photon counting techniques together with a Tennelec/Nucleus MCS II multichannel scaler card. Measurement data were analyzed using Microcal Origin 3.5 software.

### 2.2. Reagents

Oxides of dysprosium$^{III}$ (99.9%), erbium$^{III}$ (99.9%), europium$^{III}$ (99.95%), gadolinium$^{III}$ (99.9%), holmium$^{III}$ (99.9%), neodymium$^{III}$ (99.9%), samarium$^{III}$ (99.9%), ytterbium$^{III}$ (99.9%) and yttrium$^{III}$ (99.9999%) were purchased from Aldrich, Koch-Light Laboratories, Ventron and Johnson Matthey. Terbium$^{III}$ chloride (99.999%), praseodymium$^{III}$ nitrate (99.9%), and ruthenium$^{II}$ tris(2,2′-bipyridine) chloride hexahydrate were products of Aldrich. Sodium persulfate (pro analysi), sodium tetraborate (pro analysi), and perchloric acid (suprapur) were products of E. Merck. Quartz-distilled water was used for the preparation of all solutions.

## 3. Results and discussion

In the presence of $Ru(bpy)_3^{2+}$ in the aqueous electrolyte, the observed cathodic EL spectrum of an oxide-covered aluminium electrode consists of two spectral lines at ca. 2 eV and 3 eV (Fig. 1) being attributed to the radiative de-excitations of $Ru(bpy)_3^{2+}$ and $Al_2O_3$ F-center, respectively. The observed spectral lines are symmetric after the conversion between wavelength and energy and they are rather broadened so a gaussian function fits reasonably to the data in both cases. The physical origin of the line-widths results from many factors, e.g. in the case of F-center emission, probably from the diffuseness of the band structure of the $Al_2O_3$ thin film. However, Fig. 1 accords with the proposed one-emitter model for the cathodic EL of $Al_2O_3$ F-center and shows that a higher resolution than that obtained with a 20 nm detector slit or further spectral corrections are not needed for the quantitative analysis of the F-center luminescence by using the integrated areas of the spectral lines.

The relation of determined intensities in the absence ($I^0$) and in the presence ($I$) of a quencher (Q) can be used for the determination of the Stern-Volmer coefficient ($K_{SV}$) for the bimolecular reaction between F* and Q (reaction 8) according to the Stern-Volmer equation (Eq. (7)) [13],

$$I^0/I = 1 + K_{SV}[Q] \tag{7}$$

$$F^* + Q \rightarrow F + Q^{(*)} \tag{8}$$

.We measured the quenching curves for ten lanthanides, Ho, Er, Nd, Pr, Dy, Gd, Tb, Yb, Eu and Sm, together with Y, and fitted linear functions to their Stern-Volmer plots (see examples in Fig. 2 and results in Table 1). In order to

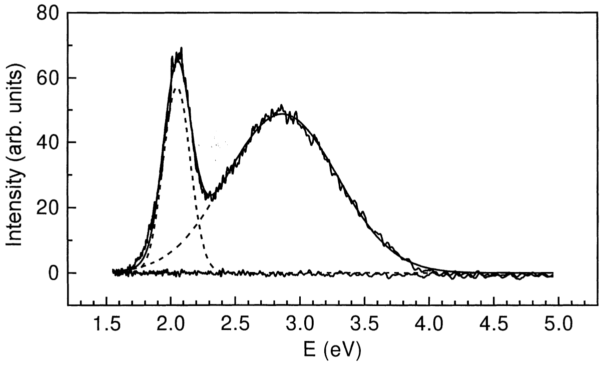

Fig. 1. Spectrum of cathodic EL of $Al_2O_3$ F-center in the presence of $3\times10^{-3}$ mol l$^{-1}$ $K_2S_2O_8$ and $4\times10^{-8}$ mol l$^{-1}$ $Ru(bpy)_3^{2+}$ in a 0.05 mol l$^{-1}$ $Na_2B_4O_7$ solution at pH 9.2.

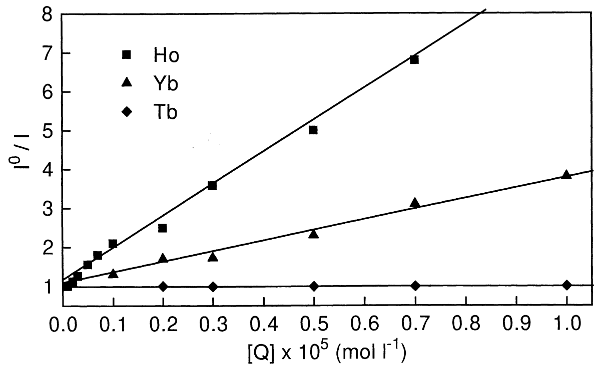

Fig. 2. Stern-Volmer plots for quenching of cathodic EL of $Al_2O_3$ F-center by different lanthanide cations at the electrode/electrolyte interface. Conditions as in Fig. 1 except without $Ru(bpy)_3^{2+}$.

Table 1
Stern-Volmer coefficients ($K_{SV}$) for the bimolecular quenching reactions between $Al_2O_3$ F-center and lanthanide (Ln) cations at the electrode/electrolyte interface

| Ln | $K_{SV}$/l mol$^{-1}$ |
|---|---|
| Ho | $8.2\times10^5$ |
| Er | $5.4\times10^5$ |
| Nd | $9.0\times10^4$ |
| Pr | $1.7\times10^4$ |
| Dy | $6.4\times10^3$ |
| Gd | $3.4\times10^3$ |
| Tb | $4.2\times10^2$ |
| Yb | $2.7\times10^5$ |
| Eu | $4.2\times10^4$ |
| Sm | $4.1\times10^3$ |
| Y | $1.5\times10^4$ |

get the values for the pseudo-first order reaction rate constants for the bimolecular quenching reactions we tried to measure the lifetime of the F-center luminescence of an $Al_2O_3$ thin film. The strongest component of the decay curve of the F-center luminescence, however, follows the decay of the cathodic excitation pulse which is known to occur in a timescale of microseconds, and thus the actual lifetime of the F-center luminescence remains unknown for us. Similarly the decay of the F-center luminescence was observed to follow the decay of the excitation pulse under conventional UV-photoexcitation. The fact that the decay of the F-center luminescence in the $Al_2O_3$ thin film is essentially faster than that in a sapphire single crystal results probably from the diffuseness of the band structure of the $Al_2O_3$ thin film. In addition to the fast component there are slower components in the decay curve of the F-center luminescence in a time scale of milliseconds (see Fig. 3). These can be attributed to the afterglow or room-temperature thermoluminescence of the $Al_2O_3$ thin film, i.e. slow feeding of the $^1P$ state or directly the emitting $^3P$ state of the F-center by electrons trapped on different trap depths within the band structure of the $Al_2O_3$ thin film.

The different quenching efficiencies of the lanthanides can be discussed taking into account that (i) $Eu^{III}$, $Yb^{III}$ and $Sm^{III}$ react rapidly with hydrated electron

$$e^-_{aq} + Eu^{3+} \rightarrow Eu^{2+} \qquad (9)$$

$$e^-_{aq} + Yb^{3+} \rightarrow Yb^{2+} \qquad (10)$$

$$e^-_{aq} + Sm^{3+} \rightarrow Sm^{2+} \qquad (11)$$

with reported second-order reaction rate constants $k_9 = 6.5\times10^{10}$ l mol$^{-1}$ s$^{-1}$, $k_{10} = 4.3\times10^{10}$ l mol$^{-1}$ s$^{-1}$ and $k_{11} = 2.0\times10^{10}$ l mol$^{-1}$ s$^{-1}$, while $Ho^{III}$, $Er^{III}$, $Nd^{III}$, $Pr^{III}$, $Dy^{III}$, $Gd^{III}$, $Tb^{III}$ and $Y^{III}$ react sluggishly or not at all with the hydrated electron [14], and (ii) the energy transfer from F* to Q (reaction 8) may take place from the $^1P$ state (energy ca. 6.1 eV) as well as from the $^3P$ state (energy ca.

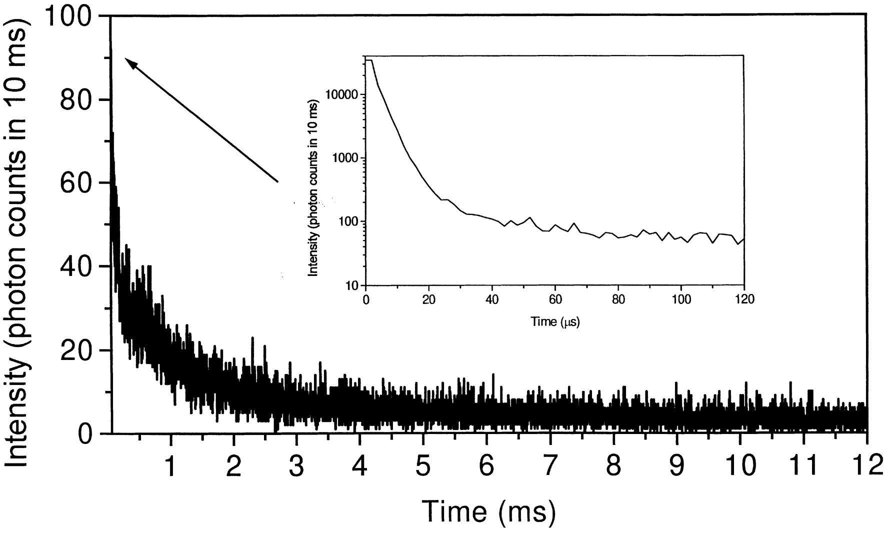

Fig. 3. Decay curve of cathodic EL of $Al_2O_3$ F-center. A sum of 5000 passes, PMT background noise is ca. 0.2 photon counts in 10 ms. Conditions as in Fig. 1 except without $Ru(bpy)_3^{2+}$. Insert: fast decay of the strongest component of the F-center luminescence.

3.0 eV) of the $Al_2O_3$ F-center. In the present conditions, the most efficient quenchers of F* are Ho, Er, Nd, Yb and Eu, as indicated in Table 1. The effects of Yb and Eu could be explained by the fact that $Yb^{II}$ and $Eu^{II}$ have considerably stronger molar absorptivities at 6.1 eV than $Sm^{II}$ (or $Gd^{III}$ or $Tb^{III}$) [15]. The quenching efficiencies of Yb, Eu and Sm seem to follow the order of the molar absorptivities of the divalent lanthanides at 6.1 eV but also closely resemble the order of the reaction rate constants of the lanthanides with the hydrated electron. The quenching efficiencies of the other lanthanides seem to follow to some extent the order of the energy gaps ($g$ in $cm^{-1}$) between the 3.0 eV F-center emission and the nearest f–f absorption transitions of the lanthanides: $g=0$, 500, 100, 800, 500, 8000 and 2600 for $^5I_8 \rightarrow {}^5G_5$, $^4I_{15/2} \rightarrow {}^2G_{9/2}$, $^4I_{9/2} \rightarrow {}^2D_{5/2}$, $^3H_4 \rightarrow {}^3P_2$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, $^8S \rightarrow {}^6P_{7/2}$ and $^7F_6 \rightarrow {}^5G_6$ transitions of Ho, Er, Nd, Pr, Dy, Gd and Tb, respectively [16]. The different oscillator strengths of the f–f transitions may also have an effect on the observed quenching efficiencies. In addition, the preparation of the stock solutions of $Ln^{III}$ by dissolving $Ln^{III}$ oxides in perchloric acid might result in small differences in perchlorate anion concentration in the sample solutions and thus the observed quenching effects by the $Ln^{III}$ cations may be disturbed by some anion effects.

$Tb^{III}$ was the only lanthanide under investigation which gave a detectable $Ln^{III}$-specific luminescence spectrum in the present conditions (Fig. 4). An electron exchange energy transfer from F* to $Tb^{III}$ (reaction 8) may occur either from the $^1P$ state (energy ca. 6.1 eV) or from the $^3P$ state (energy ca. 3.0 eV) of the $Al_2O_3$ F-center because the states lie appropriately above the $4f^75d$ and 4f* ($^5D_4$) excited states of $Tb^{III}$, respectively, (Fig. 5). The excitation of $Tb^{III}$ at its intershell $4f^8 \rightarrow 4f^75d$ absorption transition (energy ca. 5.6 eV) is much more effective than the excitation of $Tb^{III}$ at its intrashell f–f absorption transitions in the range ca. 2.5–4.1 eV [17], but the lower energy transfer pathway should also be favourable analogously to the ligand triplet state- $Tb^{III}$($^5D_4$) sensitization in the case of aromatic $Tb^{III}$ chelates [1]. In conclusion, our observations can be taken as a sign of different energy transfer rates of lanthanide cations at an oxide-covered aluminium cathode. Further investigations on this subject are in progress.

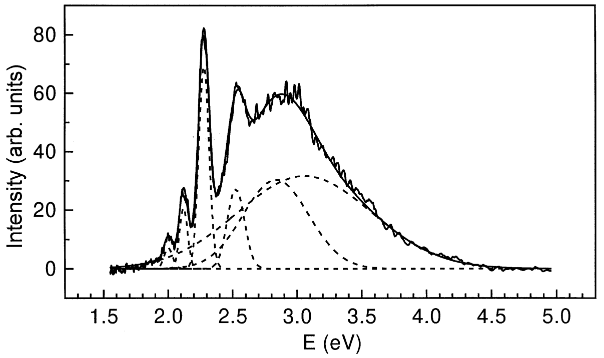

Fig. 4. Spectrum of $Tb^{III}$-enhanced cathodic EL of $Al_2O_3$ F-center. Conditions as in Fig. 1 except $Ru(bpy)_3^{2+}$ is replaced by $10^{-4}$ mol $l^{-1}$ $TbCl_3$.

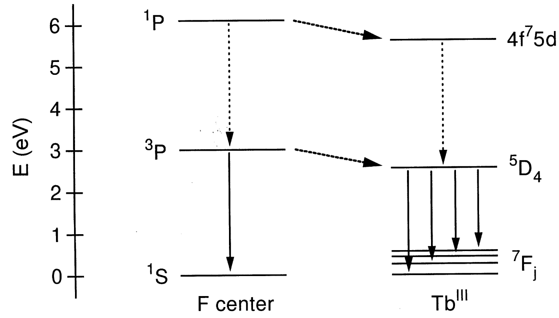

Fig. 5. Energy diagram of $Tb^{III}$-enhanced cathodic EL of $Al_2O_3$ F-center.

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