

Photo- and electroluminescence properties of lanthanide tungstate-doped porous anodic aluminum oxide



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ABSTRACT

A new cathode material for the potential use in light-emitting devices, based on porous anodic alumina (PAA), aluminum and ITO layers has been synthesized. Porous alumina samples with ordered pore arrays were prepared electrochemically from high purity Al sheet in H₂SO₄ and H₃PO₄. To be able to apply the matrix obtained in the electroluminescence cell, the thickness of the barrier layer of aluminum oxide was decreased by slow reduction of the anodization voltage to zero. The luminescence and electroluminescence (EL) properties of the Al₂O₃ matrix admixed with Eu³⁺ and Tb³⁺ ions as well as europium and terbium tungstates, were determined. The particles of inorganic luminophore were synthesized on the walls of the matrix cylindrical nanopores in the two-step process of immersion in solutions of TbCl₃ or EuCl₃ and Na₂WO₄. The effect of the nanopores diameter and the thickness of the porous Al₂O₃ layer on the intensity and relative yield of electroluminescence was analyzed, the best results were obtained for 80–90 μm PAA layers with 140 nm nanopores.

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1. Introduction

The methods for fabrication of porous alumina membranes have been known since the 1950s [1]. The oxide structures obtained as a result of anodic oxidation of aluminium in an acidic environment show very interesting physicochemical properties. The highly ordered lamellar structure of porous alumina has been applied in many areas of science and technology [2,3], in particular in electronics and biology [4], synthesis of nanomaterials, anticorrosion protection, in construction of many opto- and magneto-electronic devices [5–9]. Lanthanide ions and in particular their inorganic complexes, showing the strongest luminescence make an attractive alternative to organic compounds in many electroluminescent devices, thanks to their photochemical stability and the emission bands of narrow spectral width [10–12]. Although the first attempts at obtaining monolayer electroluminescent structures containing polyoxometaloeuropate lattices [13] have been successful, the structures obtained have not been widely applied, mainly because of the necessity of high voltage supply. A layer of porous alumina of pore diameters ranging from 15 to 200 nm is an

ideal template for luminophores, metal nanowires, enzymes and semiconductors fabricated by alternative current electrodeposition or a solution reaction into hexagonal channels of PAA [14–17]. Moreover, the physicochemical properties of anodized Al₂O₃ cause Coulomb blockade effects under single-electron transport between nanoscale surfaces and enhance chemical activity and electron emissivity of organic luminophores [11]. To the best of our knowledge, there has been no literature reports on the internal electroluminescence of lanthanide complexes with inorganic ligands in the porous Al₂O₃ film.

As yet there are no reports on internal electroluminescence of the lanthanide complexes with inorganic ligands in the Al₂O₃ layer. The preliminary results presented in this paper indicate a possibility of EL generation in the Al₂O₃ matrix with the use of europium and terbium complexes as emitters for a future application in a laminar electroluminescence device.

2. Experimental

2.1. Preparation of the PAA

Experimental procedures for the formation of self-ordered alumina are described in detail by many authors [18–22]. Aluminium plates of high purity (99.999%, Sigma – Aldrich) were

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heated in argon atmosphere up to 500 °C for 3 h and then subjected to electrochemical polishing with HClO₄ + ethanol at v:v 1:9. The process of anodic oxidation was performed in two steps in potentiostatic conditions in a solution of H₂SO₄ or H₃PO₄ at 5.0° C. The meso- and micropore diameters (C_p) were found from Equation (1) [18].

$$C_p = \sqrt{\frac{2\sqrt{3} \cdot P}{\pi}} \cdot k \cdot U \quad (1)$$

where: P – porosity (in optimal conditions P = 0.1), k – proportionality constant ≈ 2.5, U – anodizing potential.

The barrier layer of alumina was removed by slow reduction of the anodization voltage to zero. The process duration was experimentally established as it depended on the voltage used in the process of porous alumina film preparation. The pore diameter values of 15 (Fig. 1) and 140 nm, were read off from the SEM micrographs. The error in diameter determination was 16 and 20% for the pores of ~15 and ~140 nm, respectively, and it was calculated as the standard deviation of the arithmetic mean.

It is generally accepted that the oxide layer thickness (Equation (2)) formed under constant potential anodizing can be calculated [18]:

$$h = k \int_0^t i(t) dt \quad (2)$$

where: i – current intensity [mA·cm⁻²]
 $k = 3.1 \pm 0.5 \cdot 10^{-6}$ [cm³·(mA·min)⁻¹] for anodization carried out in H₂SO₄ and $k = 8.7 \pm 0.4 \cdot 10^{-6}$ [cm³·(mA·min)⁻¹] in H₃PO₄

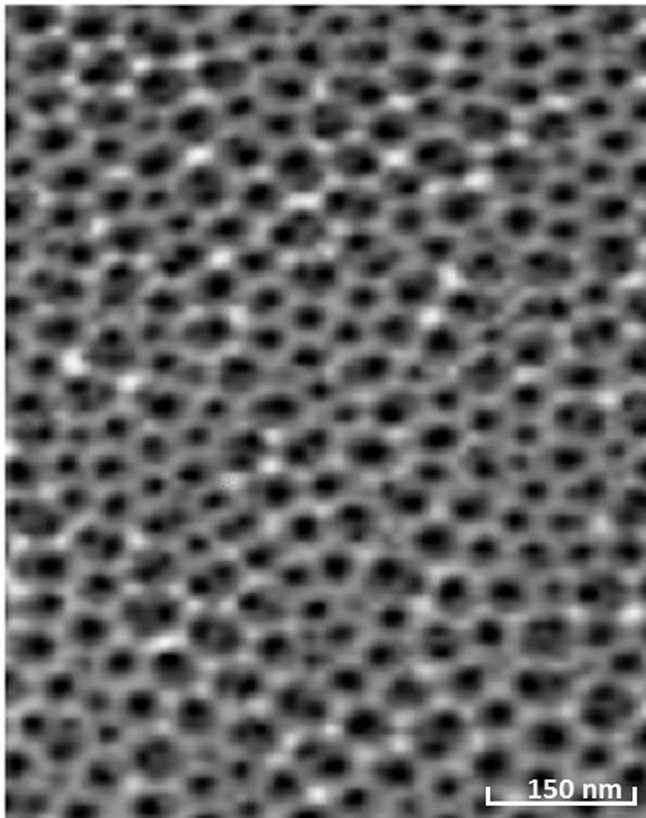


Fig. 1. Scanning electron micrograph of the anodic alumina film formed in 1.0 M H₂SO₄ solution at 21 V anodizing potential.

By anodizing oxidation of aluminium the PAA samples were produced with the porous film thickness of 15, 30, 50, 70 and 90 μm in 0.5 M of H₂SO₄ and of the thickness of 15, 40, 80, 120 and 140 μm in 1.0 M of H₃PO₄. The mean thickness of porous aluminum oxide was measured experimentally for each sample. After completion of anodization, the porous layer of aluminum oxide was separated from metallic aluminum in the saturated HgCl₂ solution. In this way porous membranes were obtained whose thickness was measured under a classical optical microscope with an ocular micrometer.

Results of microscopic measurements were compared with theoretical values and are presented in Table 1.

2.2. Synthesis of the electroluminophore

Electroluminophore was obtained with the use of europium chloride EuCl₃·6H₂O or terbium chloride TbCl₃·6H₂O (99.99% Sigma-Aldrich) and sodium tungstate Na₂WO₄·2H₂O (99.995% Sigma-Aldrich) by the two-step method inside the alumina matrix [18]. The Al plate coated with a porous alumina layer Al₂O₃ was immersed in alcohol solutions of EuCl₃ or TbCl₃ (0.2 M) for 10 h. After that the foil was carefully washed in demineralised water, dried in vacuum and immersed in a water solution of Na₂WO₄ (0.5 M) for 5 min. The process of impregnation in solutions of the lanthanide ions and the ligand was repeated a few times. The duration of the process was chosen to ensure the maximum filling. The template with europium tungstate or terbium tungstate was washed for a few times with water and ethanol and dried in vacuum at room temperature.

The formation of PAA layer admixtures with lanthanide ions was verified by the spectrofluorometric method, on the basis of the presence of emission bands characteristic of f-f electron transitions of europium and terbium ions. The effective surface area of the template was 1.2 cm². Electroluminescent cells were made of the filled porous alumina film and the ITO plate (8–12 Ω/sq) by pressing them in a special Teflon chamber. A scheme of the obtained ECL device is given in Fig. 2.

2.3. Instruments

Emission measurements were made on a spectrofluorimeter Hitachi F7000. Luminescence of weakly emitting systems was recorded by the single photon counting method with a cooled photomultiplier R636-10 Hamamatsu and a monochromator Triax 180 or a cut-off filters setup. The excitation source was a 1000W xenon lamp combined with grating monochromator (1200 grooves/mm and focal length 300 nm) and nitrogen pulse laser KEN - C6020 (wavelength 337.1 nm, pulse energy 300 μJ/10 Hz. The power supply for EL cell was a generator of rectangular pulses of regulated amplitude (0–160 V) and frequency (1–200 Hz).

Table 1

Comparison of the thicknesses of porous Al₂O₃ layers determined by anodization and calculated from Eq. (2).

| Electrolyte | Thickness of porous Al ₂ O ₃ microlayer | |
|--------------------------------|---|--------------|
| | Calculated | Observed |
| H ₂ SO ₄ | 15.4 ± 2.4 | 15.2 ± 3.2 |
| H ₂ SO ₄ | 31.2 ± 4.1 | 28.5 ± 7.0 |
| H ₂ SO ₄ | 48.6 ± 6.5 | 53.8 ± 9.3 |
| H ₂ SO ₄ | 73.0 ± 10.8 | 68.4 ± 12.2 |
| H ₂ SO ₄ | 90.4 ± 14.1 | 85.9 ± 15.7 |
| H ₃ PO ₄ | 14.8 ± 2.0 | 15.6 ± 3.4 |
| H ₃ PO ₄ | 44.2 ± 4.6 | 41.6 ± 5.0 |
| H ₃ PO ₄ | 83.8 ± 8.9 | 77.8 ± 9.0 |
| H ₃ PO ₄ | 118.6 ± 11.8 | 114.3 ± 12.6 |
| H ₃ PO ₄ | 148.9 ± 14.2 | 148.0 ± 16.6 |

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