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# Effect of aluminum annealing on the galvanoluminescence properties of anodic oxide films formed in organic electrolytes

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## Abstract

The galvanoluminescence (GL) properties of anodic oxide films formed in organic electrolytes were investigated at different aluminum annealing temperatures. The results of the spectral measurements showed two different types of GL sources: carboxylate ions incorporated in oxide films during the anodization and the molecules AlH, AlO, Al<sub>2</sub>, AlH<sub>2</sub>, also formed during anodization process and already recognized in the case of inorganic electrolytes. The latter was related to gamma alumina crystalline regions formed by annealing of the aluminum samples at temperatures above 500 °C.

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**Keywords:** Galvanoluminescence; Anodic aluminum oxide; Aluminum; Annealing

## 1. Introduction

Two types of anodic oxide films can be formed in anodization processes on an aluminum sample: barrier and porous [1]. The type of oxide film is primarily determined by the type of electrolyte. When an aluminum sample is anodized in neutral or alkaline solutions (pH > 5), a compact barrier oxide film is formed on aluminum. Their thickness is limited to several hundred nanometers due to the dielectric breakdown initiated during film growth [2]. Typical electrolytes, which form a barrier oxide film, are neutral boric acid, ammonium borate, ammonium tartrate, citric acid, tartaric acid, malic acid, succinic acid, etc. Porous oxide films are commonly formed by anodization of aluminum samples in acidic aqueous electrolytes, e.g. oxalic acid, sulfuric acid, phosphoric acid, etc. Such films consist of two regions: an outer region of thick porous-type aluminum oxide and a thin, compact inner region lying adjacent to the metal. The thickness of porous oxide films can grow to hundreds of microns [3].

Anodization of aluminum in the aforementioned electrolytes is followed by emission of a weak electromagnetic radiation, mostly in the visible region of the spectrum. This process

is termed galvanoluminescence (GL) or electroluminescence [4,5]. Since the discovery of GL in 1898 by Braun [6], it has been investigated by many authors, but explanations of the nature and the mechanism of GL are still incomplete. GL depends on many factors such as the type of electrolytes (organic or inorganic) [7], metal impurities in aluminum [8,9], surface pretreatment [10–13] and anodizing conditions (current density, temperature and concentration of electrolyte) [7,11–13].

Surface pretreatment of aluminum samples (surface preparation and annealing) has a significant influence on GL obtained in inorganic electrolytes. In fact, the pretreatment of the samples governs the concentration of “flaws” in oxide films, which are related to the GL mechanism [10–13]. “Flaws” is a general term for microfissures, cracks, local regions of different compositions and impurities, etc. [14]. The annealing temperature of the samples is another pretreatment factor that affects the GL intensity [11–13]. Higher annealing temperature results in higher GL intensity. Annealing at different temperatures has different influences on the state of a sample’s surface, number of defects, crystal grains and their orientation, in other words, on the concentration of “flaws”. We showed that the GL spectra of barrier and porous oxide films formed in inorganic electrolytes had the same shape (two spectral peaks at about 430 nm and 600 nm, respectively). This fact clearly indicates the same origin of GL in all inorganic electrolytes [15]. Our recent investigation of GL of oxide films formed by anodization of aluminum samples

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annealed at temperatures above 500 °C in inorganic electrolytes, has shown that the sudden rise in the formation of gamma crystalline regions caused by aluminum annealing is strongly related to the appearance of GL and its intensity. GL intensity is about two orders of magnitude more intense for 550 °C-annealed samples than for samples annealed below 500 °C [16]. We recorded the GL spectra and observed six intensive and broad emission bands with peaks around 430 nm, 483 nm, 544 nm, 575 nm, 601 nm and 648 nm. A semi-quantitative analysis based on literature data on simple molecular species involving the Al atom, as well as those atoms whose presence was possible under given experimental conditions (hydrogen, oxygen, etc.), showed that sources of GL are molecules AlH, AlO, Al<sub>2</sub> and AlH<sub>2</sub>, related to the formation of gamma alumina crystal islands at annealing temperatures above 500 °C.

Tajima et al. suggested that carboxylate ions incorporated in the oxide films during the anodization in the organic electrolytes acted as the GL centra [7]. GL in organic electrolytes is attributed to deexcitation of the GL centra excited by electrons of the electron avalanche formed in a high electric field (nearly 10<sup>7</sup> V/cm) during aluminum anodization [17,18]. Our recent GL spectral measurements confirmed the assumption that carboxylate ions were the GL centra in organic electrolytes, which form barrier and porous oxide films [19].

The aim of this paper was to investigate the influence of flaws generation caused by aluminum annealing at different temperatures, especially at temperature above 500 °C, on the GL properties of anodic oxide films formed in organic electrolytes.

## 2. Experimental

Anodic oxide films were formed on a high-purity cold-rolled aluminum (99.999% obtained from Goodfellow) sample of dimensions 25 mm × 10 mm × 0.12 mm. The aluminum anodization was carried out in a vessel with flat glass windows. Platinum wires were used as cathodes. The electrolyte was thermostated at a certain temperature. The electrolyte circulated through the chamber-reservoir system, and the control temperature sensor was situated immediately by the sample. The temperature of the electrolyte was maintained during anodization to within 0.1 °C. For aluminum anodization, we used water solutions of 0.1 M citric acid, tartaric acid, malic acid, succinic acid, ammonium tartrate, and oxalic acid. The electrolytes were prepared using double distilled, deionized water and PA grade chemical compounds. The aluminum samples were annealed for 5 h at various temperatures (350 °C, 450 °C, 500 °C and 550 °C) and then slowly cooled. The aluminum surface was prepared for anodization in three ways: (a) electropolished in HClO<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH solution (1:4, v/v) following the procedure given by Tajima et al. [7], rinsed with ethanol and dried; (b) chemically cleaned in the bath consisting of 20 g/l chromium trioxide and 35 ml/l concentrated phosphoric acid at 80 °C for 30 min followed by rinsing in distilled water and dried; (c) just degreased in ethanol by using ultrasonic cleaner. The surface of aluminum after annealing was characterized by scanning electron microscope (SEM) JEOL 840A and Bruker D8 Advance Diffractometer.

GL measurements were performed utilizing two optical-detection systems. To investigate the influence of aluminum annealing on GL intensity we used a monochromatic measuring system consisting of a large-aperture achromatic lens, an optical monochromator of a rather high luminosity (Zeiss SPM-2), and a very sensitive cooled (at approximately –40 °C) photomultiplier (RCA J1034 CA). The optical-detection system was calibrated using a standard tungsten strip lamp (Osram Wi-17G). The intensity of GL, the voltage of anodization and the temperature of electrolyte were recorded by 20-channel digital PC-controlled multimeter HP 34970A.

Spectral GL measurements were performed utilizing a spectrograph system based on the Intensified Charge Coupled Device (ICCD) camera intended for time-resolved measuring of very weak light intensity in a wide range of wavelengths. The optical and detection system consisted of a large-aperture achromatic lens, a Hilger spectrograph with diffraction grating GR50-0305 (300 grooves/mm, blaze at 500 nm and angular dispersion 3.32 nm/mrad) and a very sensitive PI-MAX ICCD cooled camera with high quantum efficiency manufactured by Princeton Instruments. The CCD chip consisted of 1024 × 256 pixels, each approximately 26 μm × 26 μm. To reduce the dark current the CCD chip is cooled at –40 °C using Peltier devices. The system is used at two grating positions with ranges from 400 nm to 560 nm and from 540 nm to 700 nm, with overlapping wavelength range from 540 nm to 560 nm. The optical-detection system was calibrated using a LED-based light source [20].

As the measuring spectral range is covered with two grating positions, two aluminum samples are needed, anodized at the same anodizing conditions (current density, voltage of anodization, temperature of electrolyte and electrolyte composition). GL spectra were recorded in shutter mode. As a relatively slow change of the voltage and GL intensity was involved, a scanning speed of one spectrum per second was fast enough for our spectral measurements. The obtained spectra were corrected to the spectral response of the measuring system.

## 3. Results and discussion

### 3.1. GL properties of porous anodic oxide films

Fig. 1 shows typical voltage versus time and GL intensity versus time characteristics for porous oxide films formed by anodization of aluminum samples annealed at 450 °C (Fig. 1a) and 550 °C (Fig. 1b) in oxalic acid. GL intensity for samples annealed at 550 °C is higher than for samples annealed at 450 °C, particularly in the early stage of anodization. We expected that gamma alumina crystalline regions, formed by aluminum annealing at temperature above 500 °C [21], were the source of additional optical radiation. Further results should confirm this assumption.

The effect of aluminum annealing on GL intensity is shown in Fig. 2. The annealing treatment of aluminum samples at temperatures below 500 °C has low influence on the GL intensity. When annealing temperatures were above 500 °C, a higher GL intensity was obtained for a higher annealing temperature. It is already known that films formed on aluminum annealed at tempera-

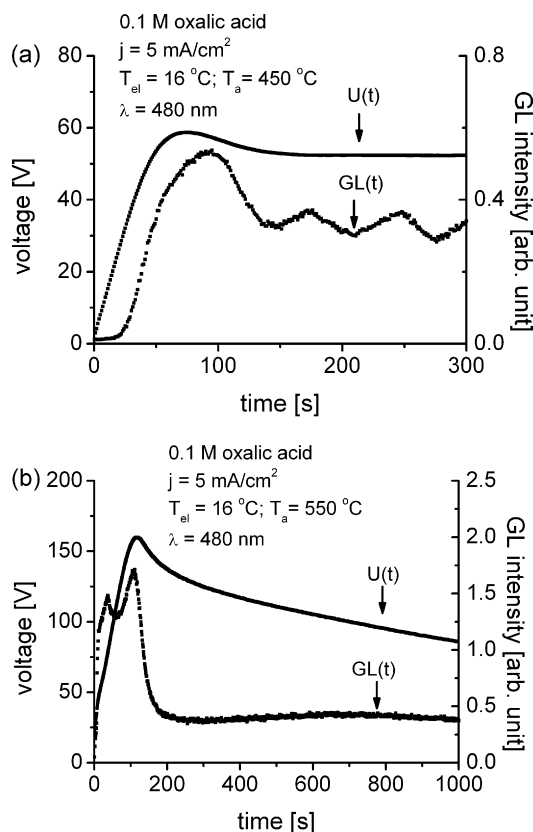


Fig. 1. Voltage–time and GL intensity–time dependence during anodization of aluminum samples annealed at (a)  $450^\circ\text{C}$  and (b)  $550^\circ\text{C}$  in 0.1 M oxalic acid ( $j = 5 \text{ mA/cm}^2$ ,  $T_{\text{el}} = 16^\circ\text{C}$ ,  $\lambda = 480 \text{ nm}$ ).

tures above  $500^\circ\text{C}$  contain large crystalline regions of gamma alumina [21], whereas films formed on aluminum annealed at temperatures below  $500^\circ\text{C}$  have an amorphous structure with possible small contents of very small crystals [22]. These facts also point to gamma alumina crystalline regions as a possible source of GL.

Fig. 3 shows the effect of surface pretreatment on porous oxide films formed by anodization of  $550^\circ\text{C}$ -annealed aluminum samples. The GL intensity is the strongest when an aluminum sample is just degreased and chemically cleaned, whereas it decreases significantly when sample is also elec-

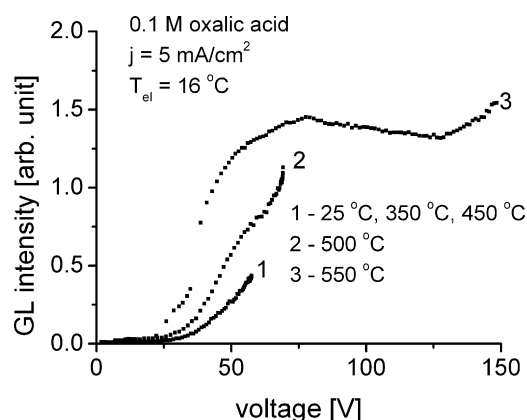


Fig. 2. Effect of temperature of aluminum annealing on GL intensity.

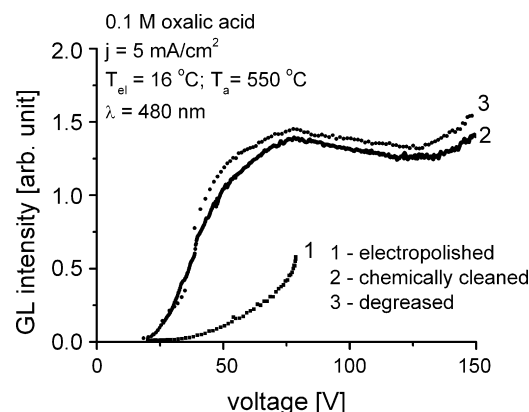


Fig. 3. Effect of the surface pretreatment of aluminum samples annealed at  $550^\circ\text{C}$  on GL intensity of porous oxide films formed in oxalic acid ( $j = 5 \text{ mA/cm}^2$ ,  $T_{\text{el}} = 16^\circ\text{C}$ ,  $\lambda = 480 \text{ nm}$ ).

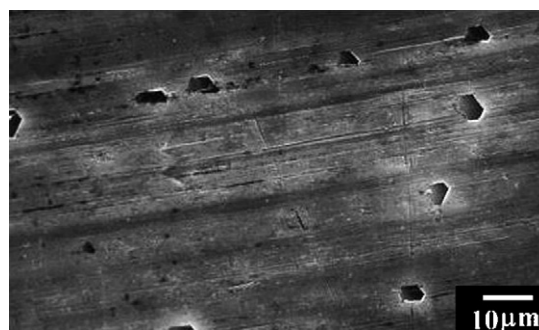


Fig. 4. SEM image of the chemically cleaned aluminum surface with crystalline islands.

tropolished. Chemical cleaning in a boiling mixture of phosphoric and chromic acids removes amorphous alumina and surface contaminants, leaving crystalline alumina relatively unattacked [23], but electropolishing almost completely removes islands of crystalline alumina. Fig. 4 shows an SEM image of a chemically cleaned aluminum surface and indicates islands of crystalline alumina. Fig. 5 shows an XRD scan of  $550^\circ\text{C}$ -annealed samples in air, which confirms our assumption that crystalline islands detected by SEM are gamma alumina crystals [24].

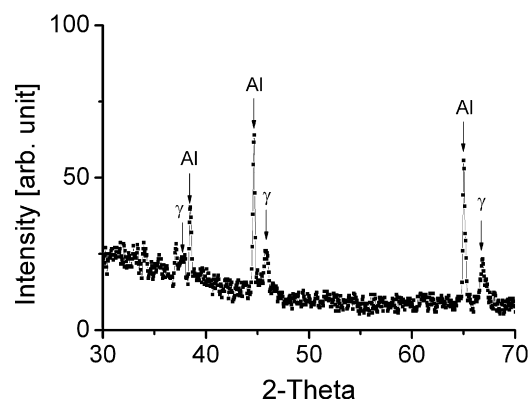


Fig. 5. XRD spectrum of aluminum samples annealed at  $550^\circ\text{C}$  in air for 5 h.

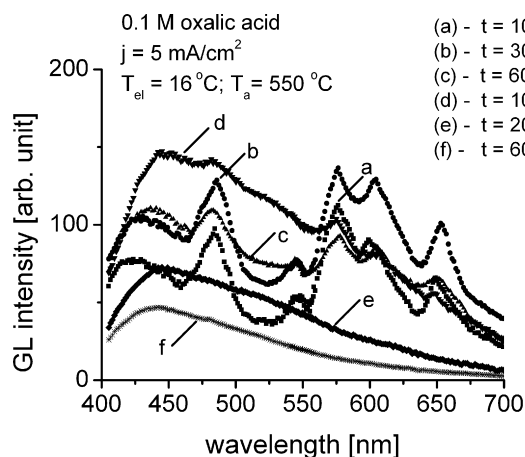


Fig. 6. Evolution of the GL spectrum with time during anodization of aluminum samples annealed at 550 °C in 0.1 M oxalic acid at a current density of 5 mA/cm<sup>2</sup> and temperature of electrolyte at 16 °C: (a) 10 s; (b) 30 s; (c) 60 s; (d) 100 s; (e) 200 s; (f) 600 s.

Fig. 6 shows the evolution of GL spectrum at 16 °C electrolyte temperature and with the constant current density of 5 mA/cm<sup>2</sup>, during anodization of 550 °C-annealed aluminum samples in 0.1 M oxalic acid. In the early anodization stage, the GL spectrum was composed of six intensive and broad emission bands with peaks around 430 nm, 483 nm, 544 nm, 575 nm, 601 nm and 648 nm (Fig. 6a and b). We obtained the same shape of the spectrum as for porous oxide films on 550 °C-annealed aluminum samples in inorganic electrolytes (phosphoric and sulfuric acid) [16]. Our analysis, already performed in the case of GL spectra in inorganic electrolytes [16], showed that spectral systems which could contribute to our spectrum recorded in the range from 400 nm to 700 nm were  $X^1A_1 \leftarrow A_1\Pi$  of AlH,  $X^2\Sigma^+ \leftarrow B^2\Sigma^+$  of AlO,  $X^3\Sigma_g^- \leftarrow A^3\Sigma_u^-$  of Al<sub>2</sub> and  $X^2A_1 \leftarrow A^2A_1(^2\Pi_u)$  of triatomic radical AlH<sub>2</sub>, possibly contained in pores of the gamma alumina crystal islands.

During aluminum anodization, porous oxide grew at the oxide/electrolyte interface because of the outward migration of aluminum ions and their reaction with oxygen-containing electrolytes species at aluminum/oxide. At the same time, the oxide at the oxide/electrolyte interface was dissolved due to field-stimulated interaction of electrolyte species with the oxide [3,25]. In porous oxide films, the light was emitted from the barrier part of porous films and the GL intensity increased with anodization voltage [26]. When electrons accelerated in the conduction band of the barrier layer oxide attained energy values necessary for the excitation of the carboxylate ions, the GL spectrum changed the shape (Fig. 6c–f). The carboxylate ions incorporated in oxide films, acted as the luminescent centra with broad GL band in the visible region and spectral peak at about 450 nm [27]. When all gamma alumina crystals completely moved from the barrier to porous part of oxide films, the GL spectrum had the same shape (Fig. 6f) as the GL spectrum of porous oxide films formed by anodization of aluminum samples annealed below 500 °C (Fig. 7). After that, carboxylate ions incorporated in oxide during the anodization remained the only source of GL.

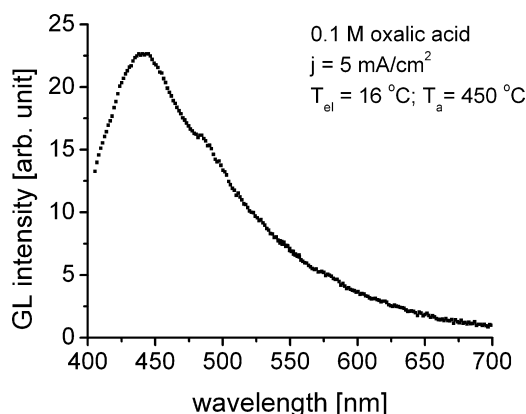


Fig. 7. GL spectrum of aluminum samples annealed at 450 °C in 0.1 M oxalic acid at a current density of 5 mA/cm<sup>2</sup> and temperature of electrolyte at 16 °C.

### 3.2. GL properties of barrier anodic oxide films

Fig. 8 shows typical voltage versus time and GL intensity versus time characteristics for barrier oxide films formed by anodization of aluminum samples annealed at 450 °C (Fig. 8a) and 550 °C (Fig. 8b) in organic electrolytes (citric acid, tartaric acid, malic acid, succinic acid and ammonium tartrate). The GL intensity for samples annealed at 550 °C was higher than for samples annealed at 450 °C. In addition, we obtained the same effect of annealing and surface pretreatment on GL intensity as for porous oxide films.

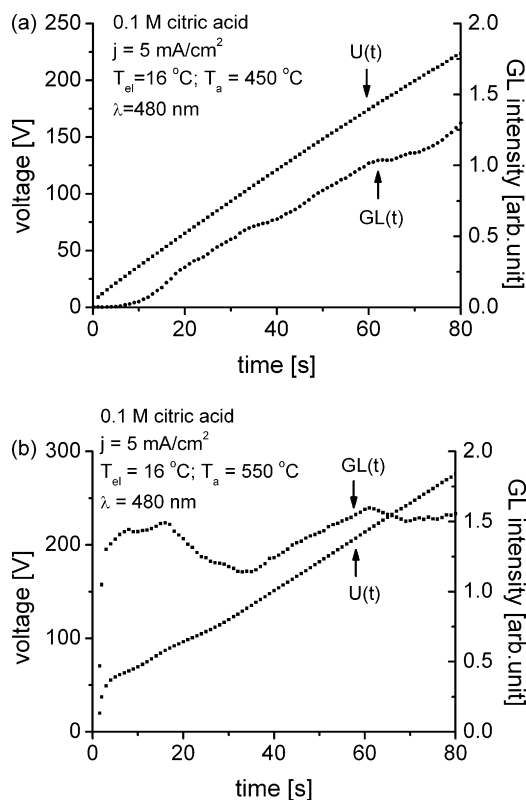


Fig. 8. Voltage–time and GL intensity–time dependence during anodization of aluminum samples annealed at (a) 450 °C and (b) 550 °C in 0.1 M citric acid ( $j = 5 \text{ mA/cm}^2$ ,  $T_{\text{el}} = 16^\circ\text{C}$ ,  $\lambda = 480 \text{ nm}$ ).



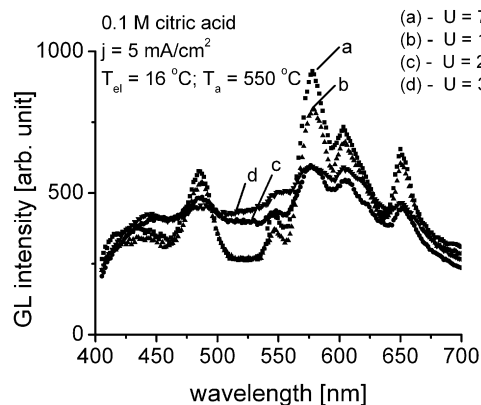


Fig. 9. Changes in the spectrum of the barrier oxide films with formation voltage during anodization of aluminum samples annealed at 550 °C in 0.1 M citric acid at a current density of 5 mA/cm<sup>2</sup> and temperature of electrolyte at 16 °C: (a) 75 V; (b) 100 V; (c) 200 V; (d) 300 V.

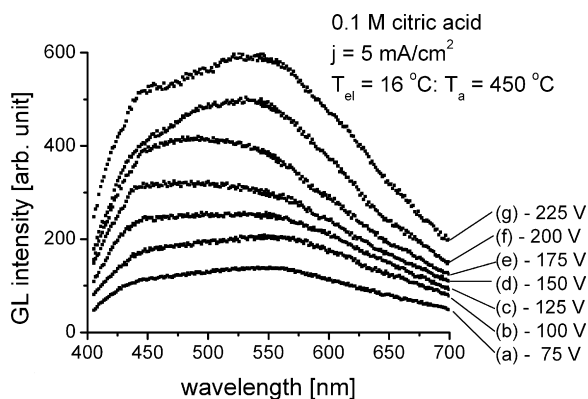


Fig. 10. Changes in the spectrum of the barrier oxide films with formation voltage during anodization of aluminum samples annealed at 450 °C in 0.1 M citric acid at a current density of 5 mA/cm<sup>2</sup> and temperature of electrolyte at 16 °C.

Fig. 9 shows the evolution of the GL spectrum at 16 °C electrolyte temperature and at a constant current density of 5 mA/cm<sup>2</sup> during anodization of 550 °C-annealed aluminum samples, in 0.1 M citric acid. The shape of spectrum was quite different from the GL of samples annealed below 500 °C (Fig. 10). These facts point out that gamma alumina crystalline regions have dominant influence on GL of barrier oxide films formed by aluminum anodization in organic electrolytes, especially for lower anodization voltage. GL spectral measurement in other organic electrolytes (tartaric acid, malic acid, succinic acid and ammonium tartrate) produced the same results.

#### 4. Conclusion

Our results show that the GL spectrum of both porous and barrier films obtained during anodization in organic electrolytes depends on the annealing temperature. When aluminum samples are annealed below 500 °C, the carboxylate ions incorporated in

the oxide films during the anodization act as luminescence centers and the only source of optical radiation obtained during the anodization process. If aluminum samples are annealed at temperature above 500 °C, the gamma alumina crystalline regions are formed resulting in the additional optical radiation originated from the transitions in the molecules AlH, AlO, Al<sub>2</sub> and AlH<sub>2</sub>, already recognized in inorganic electrolytes. As a result, the obtained GL spectrum is composed of optical radiation from two sources: the carboxylate ions and the aforementioned molecules.

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