

# Nanoporous Materials through Anodizing of Iron in F-containing Organic Electrolytes

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## ABSTRACT

In this study, our recent progress in fabrication, characterization and application of thick nanoporous anodic films is presented and discussed. Scanning electron microscopy (SEM), X-ray diffraction, Mössbauer and X-ray photoelectron spectroscopy (XPS) combined with thermo gravimetric analysis (TGA) have been here applied to detect compositional and structural differences of film layers formed at the metal/film interface and at the surface side. We have found that *Etg*-NH<sub>4</sub>F films, are constructed mainly of lepidocrocite ( $\gamma$ -FeOOH) with some FeF<sub>2</sub> while DMSO-H<sub>2</sub>SiF<sub>6</sub> ones are mainly composed of akaganeite ( $\beta$ -FeOOH), stabilized with fluoride ions, and FeF<sub>2</sub> with some FeF<sub>3</sub> and silica hexafluorides. Notice that calcination process to hematite is sufficiently hampered for DMSO-H<sub>2</sub>SiF<sub>6</sub> films probably due to the stabilization effect of fluoride ions.

**Keywords:** nanoporous materials, iron anodizing, characterization, calcination

## 1 INTRODUCTION

The formation of either nanoporous or nanotubular films onto the surface of pure iron of thickness of several micrometers has been reported in F-containing glycerol and ethylene glycol (*Etg*) solutions only just several years ago [1-4]. Recently, through optimization of anodizing conditions in *Etg* electrolyte nanoporous anodic films of thickness of up to 10-13  $\mu$ m have been prepared and transformed to prospective hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) by a simple calcination protocol at 500 °C. Following our recent study [5], nanoporous films can also be produced by anodizing of iron in dimethyl sulphoxide (DMSO) electrolyte containing silica hexafluoride acid. Contrary to *Etg*-NH<sub>4</sub>F-H<sub>2</sub>O electrolyte, we have found that DMSO – H<sub>2</sub>SiF<sub>6</sub> process allows fabrication of extremely thick bi-layered films attaining 50  $\mu$ m and more just during one hour. Although cracked on drying and annealing these films were found to be well adherent to the substrate and not cracked at the metal/film interface.

The aim of this work is to study the composition of nanoporous anodic films grown by iron anodizing in F-containing *Etg* and DMSO electrolytes using Mössbauer,

wave dispersive X-ray (WDX) and X-ray photoelectron (XP) spectroscopies. Peculiarities of calcination of these films by heat-treatment in air are also presented and discussed.

## 2 EXPERIMENTAL

Iron foil (99.9 wt%, 0.127 mm thick), ethylene glycol and dimethyl sulphoxide were purchased from Sigma-Aldrich Chemicals Inc. DMSO was reagent grade with water content  $\leq$  0.01%. Chemically pure H<sub>2</sub>SiF<sub>6</sub> (45 %), CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH (EtOH) were purchased from Russia and used as received. For current transient investigations, a short high purity (99.9 wt%) iron rod of 4.37-mm-diameter was press-fitted into a shroud of Teflon to provide a planar, circular electrode with an area of 0.15 cm<sup>2</sup>. Prior to anodizing, the surface of electrodes was ultrasonically cleaned in acetone, EtOH and deionized distilled (DD) water baths, in each for 3 min, and dried.

The specimens were anodized in the one-compartment thermostated bath of 75 cm<sup>3</sup> volume. A sample was positioned vertically between two stainless steel or Pt plates as cathodes at a distance of  $\sim$ 13 mm from each other. For anodizing, a direct current supply at a constant bias potential ranging from 10 to 100 V was used. The anodizing solution was stirred by a rotating magnet (2.5 g; 2.5 cm; BRAND®) at about 100 rms and its temperature was fixed by Lauda®. Following anodizing, the specimens were carefully rinsed either in several EtOH or DD water baths, then dried and placed in desiccators for subsequent compositional and structural investigations. Every specimen was anodized in freshly prepared solution. For annealing of anodized specimens the programmable muffle (Zhermack®, Italy) was applied using 10 °C/min temperature ramp, up to 500 °C temperature and annealing time up to 10 hours.

A scanning electron microscope model EVO-50 (Carl Zeiss, 2005) equipped with the WDX and EDX spectrometers was applied to investigate the morphology and elemental analysis of as-grown and calcinated films. Thermogravimetry (TG) and differential thermal analysis (DTA) were conducted using the TA Instruments Thermogravimetric analyzer (LINSEIS STA Platinum 1600). The formed product was carefully scraped from the iron substrate, dried in desiccators for several days,

powdered, and loaded into the sealed alumina pan for dynamic heat-treatment at temperature from ambient to 1000 °C at a heating rate of 10 °C/min. The empty Al<sub>2</sub>O<sub>3</sub> pan was used as reference and the heat flow between the sample and reference pan was recorded.

Mössbauer spectra (MS) were taken in the transmission geometry using the source of <sup>57</sup>Co(Rh). For low temperature measurements a closed cycle He cryostat (Advanced Research Systems, Inc) was used. The spectra were fitted using WinNormos (Site@Dist) program software. Discrete sextet, singlet and doublet subspectra were fitted to the room and low temperature Mössbauer spectra.

### 3 RESULTS AND DISCUSSION

#### 3.1 Ethylene glycol solutions

Figure 1 shows the current transients for anodizing of iron in Etg solutions containing some NH<sub>4</sub>F and H<sub>2</sub>O at various bath voltages ( $U_a$ ) and temperatures. As seen, the  $j_a(t)$  plots obtained for various  $U_a$  look qualitatively similar, differing only negligibly with  $U_a$  variables, while a sharp current peak at the beginning of anodizing strongly depends on the magnitude of anodic potential. Also, a much stronger effect on the anodic oxidation is seen upon increase in the solution temperature (inset in Fig. 1) and concentration of fluoride. As far as stirring is concerned, interesting results were obtained. When the solution was vigorously stirred, some parts at the electrode corners remained uncovered. Moreover, in the case of anodizing without electrolyte stirring, 25 to 50 % higher current densities were obtained. It appears that the stirring results in more porous surface formation under the same anodizing conditions. It is noteworthy that in this electrolyte quite uniform anodic films coloured from gold to cherry tints can be obtained within the 20 to 100 V range, although the quality and thickness of films varied significantly with  $U_a$ .

The typical morphology of Etg films is shown in Figure 2. In line with [4] we also note that both nanochannel and nanotubular films can be grown in Etg electrolytes, depending on the  $U_a$  and  $T_a$  values. An increase in processing time ( $t_a$ ) results in the formation of a thicker film, while increase in  $U_a$  led to the formation of a more porous structure. Also, the diameter of each nanochannel ( $\varnothing$ ), oriented mainly perpendicular to the substrate, varied distinctly. For 60 V films, the diameter  $\varnothing = 92 \pm 10$  nm and the wall thickness,  $l = 60 \pm 7$  nm. The thickest films, attaining 10-12  $\mu\text{m}$ , were obtained at 15 °C and  $U_a$  40 V after 2.5 h anodizing in the solution containing 0.15 wt% NH<sub>4</sub>F and 20 cm<sup>3</sup> dm<sup>-3</sup> H<sub>2</sub>O under mild stirring conditions.

To estimate the composition of as-grown anodic films onto the iron surface in Etg-NH<sub>4</sub>F-H<sub>2</sub>O solutions at various bath voltages, Mössbauer spectroscopy was applied. Room temperature (RT) Mössbauer spectra (MS) recorded in the conversion electron mode are depicted in Figure 3. As seen,

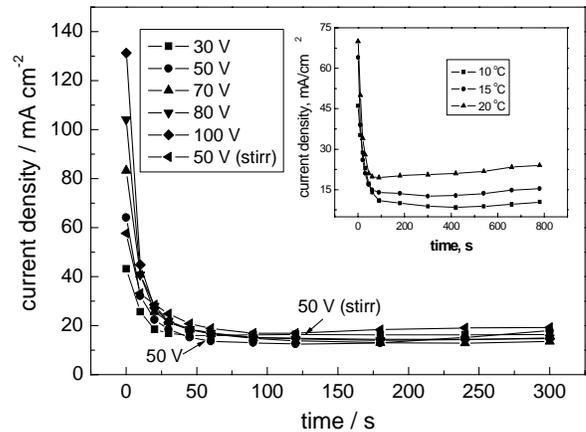


Figure 1: Current transients  $j_a(t_a)$  during anodization of iron surface in an Etg electrolyte containing 0.15 wt% NH<sub>4</sub>F and 20 cm<sup>3</sup> dm<sup>-3</sup> H<sub>2</sub>O at 15 °C and indicated voltages. Inset demonstrates the same  $j_a(t_a)$  plots for Fe anodizing at 50 V and indicated bath temperatures.

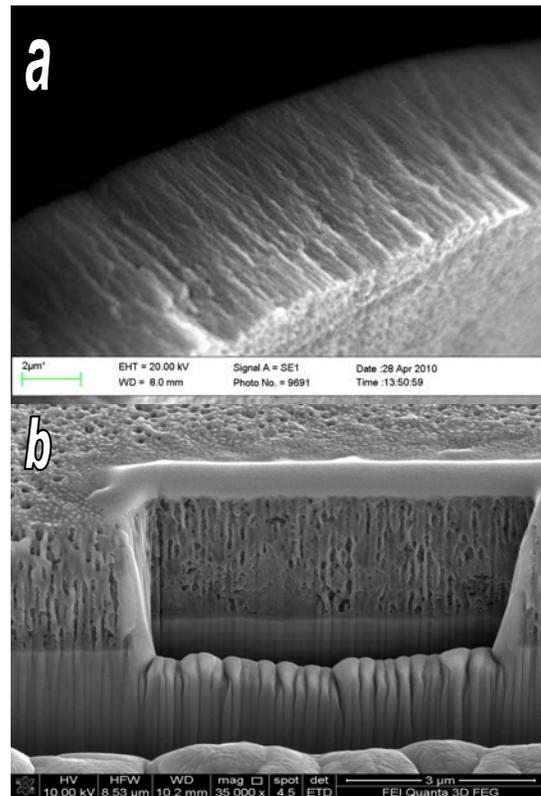


Figure 2: In-plane SEM views of anodic oxide films produced by Fe anodizing in the same electrolyte as in Fig. 1 at the bath voltages: (a) 40; (b) 60 V.

the central part of each MS can be fitted with up to three doublets. For films formed at lower applied voltages, c.a. at  $U_a = 40\text{-}50$  V, the doublet with the isomer shift,  $\delta = 1.1\text{-}1.2$  mm/s, and quadrupole splitting,  $\Delta = 3.1\text{-}3.2$  mm/s, was

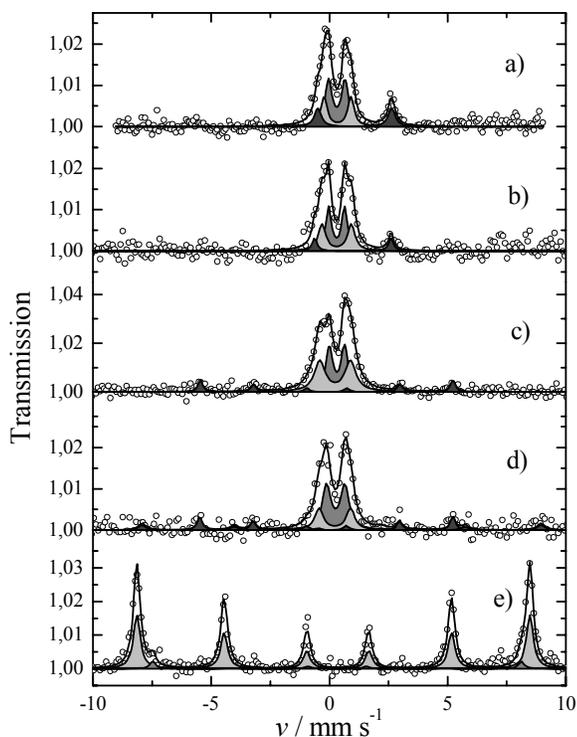


Figure 3: RT conversion electron MS of iron samples anodized in Etg solution containing 0.15 wt%  $\text{NH}_4\text{F}$  and  $20 \text{ cm}^3 \text{ dm}^{-3} \text{ H}_2\text{O}$  at  $15 \text{ }^\circ\text{C}$  and dc bias voltage: (a) 40, (b) 50, (c) 75, (d) 100 V. (e) the same MS for specimen anodized at 75 V after 2 h heating at  $500 \text{ }^\circ\text{C}$ .

attributed to Fe(II) while the other two doublets were used for description of Fe(III) contributions [6]. When fitting conversion electron MS, the hyperfine parameters for Fe(III) doublets:  $0.37\text{-}0.42 \text{ mm/s}$ ,  $\Delta = 0.63\text{-}0.77 \text{ mm/s}$  and  $\delta = 0.36\text{-}0.45 \text{ mm/s}$ ,  $\Delta = 1.1\text{-}1.3 \text{ mm/s}$ , respectively, were obtained. According to these hyperfine parameters the iron anodic film may consist of Fe(III) paramagnetic at RT or superparamagnetic compounds: iron oxides, hydroxides or oxyhydroxides. Measurements at cryogenic temperatures helped us to distinguish which of possible Fe(III) compounds compose the anodic film. Referring to hyperfine field  $B = 45.4 \text{ T}$ , of the sextet which is seen together with the sextet of iron in the MS of the specimen collected at a cryogenic temperature, c.a.  $14 \text{ K}$ , it should be attributed to lepidocrocite,  $\gamma\text{-FeOOH}$  [6,7].

### 3.2 Dimethyl sulfoxide solutions

Contrary to titanium, no significant film formation can be achieved by iron anodizing in the DMSO electrolyte containing HF. However, we have found that in the DMSO electrolyte with silica hexafluoride acid the growth of the passive film proceeds on the iron surface uniformly and effectively within a distinct region of  $\text{H}_2\text{SiF}_6$  concentrations and anodizing cell potentials. Typical current transients of iron anodizing process in the DMSO electrolyte are shown

in Figure 4. As seen, application of a constant anodizing cell potential regime results in an abrupt increase in the current for a very short time followed by a sharp current decay obviously depending on  $C_{\text{H}_2\text{SiF}_6}$ . The development of the passive film in the DMSO electrolyte containing  $\text{H}_2\text{SiF}_6$  with progress in anodizing time was examined further in detail by using a series of specimens and 30 V dc bias, which is ascertained as optimal. The obtained results are presented in the *Inset* of Figure 4. The respective rate of the film thickness increase in the solution containing  $30 \text{ cm}^3 \text{ dm}^{-3} \text{ H}_2\text{SiF}_6$  was approximated to  $0.9 \pm 0.1 \text{ } \mu\text{m/min}$  within  $10 \leftrightarrow 60 \text{ min}$  of the processing time. Hence, the anodic films of thickness of up to  $50 \text{ } \mu\text{m}$  and even thicker can be formed.

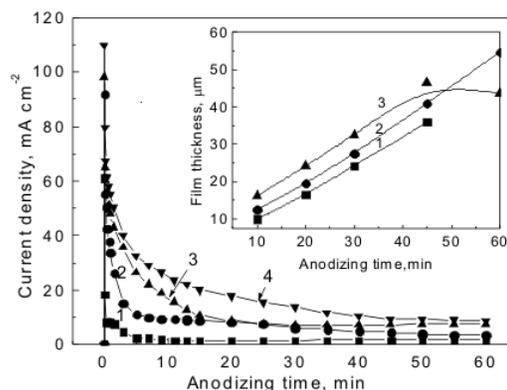


Figure 4: Current transients of iron anodizing in the DMSO electrolyte containing: (1) 10; (2) 20; (3) 30 and (4)  $40 \text{ cm}^3 \text{ dm}^{-3} \text{ H}_2\text{SiF}_6$  at 30 V and  $25 \text{ }^\circ\text{C}$  for 60 min. The *Inset* presents variations of the anodic film thickness under the same anodizing conditions for DMSO electrolytes containing (1) 20; (2) 30 and (3)  $40 \text{ cm}^3 \text{ dm}^{-3} \text{ H}_2\text{SiF}_6$ . The film thicknesses are the averaged data of ten measurements.

The morphology of films formed by iron anodizing in the DMSO- $\text{H}_2\text{SiF}_6$  electrolyte is surprising due to the bi-layered structure and crack design (Figure 5). An outer gel layer of this film is colored in cherry and cracks when drying. The contents of the main elements, namely Fe, O, F and Si, which compose film material, were found differ significantly at the metal/film and the outer gel layer, which contains more fluoride and less iron. However, from the analytical results it was difficult to determine the exact composition of layers.

The low temperature Mössbauer spectra collected for as-grown iron anodic films and washed in water were successfully fitted using three sextets with fixed quadrupole shifts:  $2\varepsilon = -0.81, -0.24, \text{ and } -0.02 \text{ mm/s}$ , obtaining hyperfine fields equalled to  $B = 48.8 \pm 0.2, 45.7 \pm 0.2 \text{ and } 48.6 \pm 0.1 \text{ T}$ , respectively. According to the data of fitting, the MS measured at  $10 \text{ K}$  for the as-grown anodic film in the DMSO- $\text{H}_2\text{SiF}_6$  electrolyte under conditions of this study shows parameters which are characteristic of akaganeite,  $\beta\text{-}$

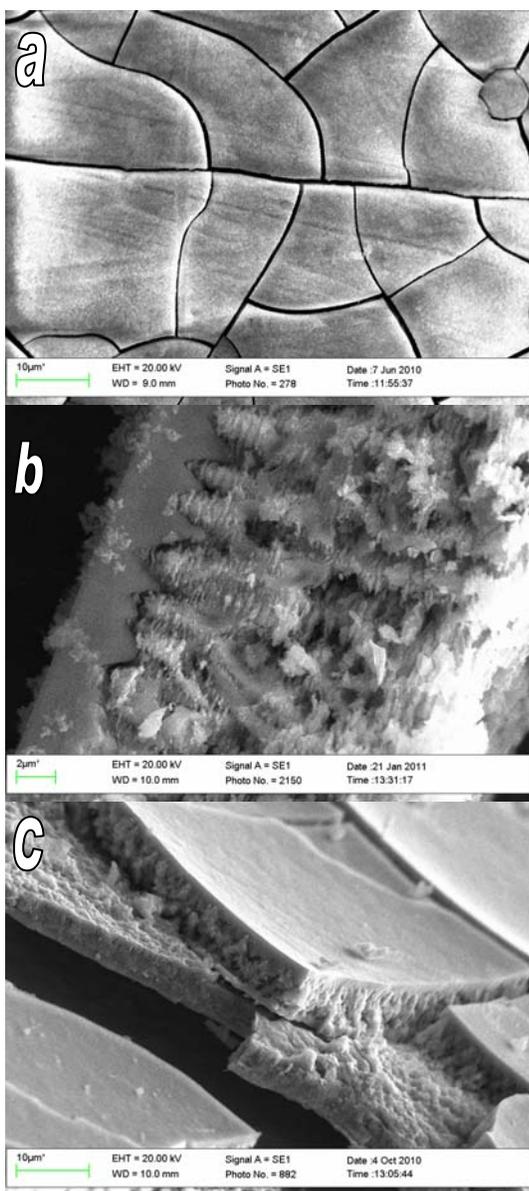


Figure 5: Typical top-side (a), cross-sectional (b) and in plane (c) FESEM view of anodic films fabricated in Etg solution containing  $\text{H}_2\text{SiF}_6$ .

$\text{FeOOH}$ . Considering the Mössbauer spectra of iron oxyhydroxides measured at temperature of 4.2 K, we note that only those of akaganeite can be fitted using several sextets with different quadrupole shifts,  $2\varepsilon$  [8]. We suggest that some part of  $\text{F}^-$  ions act here as stabilizers of akaganeite structure while other ones contained mainly in  $\text{FeF}_2$ . This conclusion was supported by MS fitting results and WDX data implying the formation of film from 53.5 % of  $\text{FeF}_2$ , 44.65 % of  $\beta\text{-FeOOH}$ , and 1.85 % of  $\text{FeSiF}_6$ .

The typical MS of the iron anodic film material after annealing at 500 °C in air are depicted in Figure 6. In this case, a considerable part of the room temperature spectrum area (~35 %) can be well fitted by sextet, having the

parameters:  $2\varepsilon = -0.22 \pm 0.01$  mm/s,  $\Delta = 0.31 \pm 0.01$  mm/s and  $B = 50.82 \pm 0.03$  T, and attributed to hematite. The other sextet (22 %), the lines of which are slightly broadened and which has nearly the same quadrupole shift ( $-0.20 \pm 0.01$  mm/s) and smaller hyperfine field ( $B = 48.4 \pm 0.2$  T), may also be attributed to hematite having smaller grains which induce superparamagnetism.

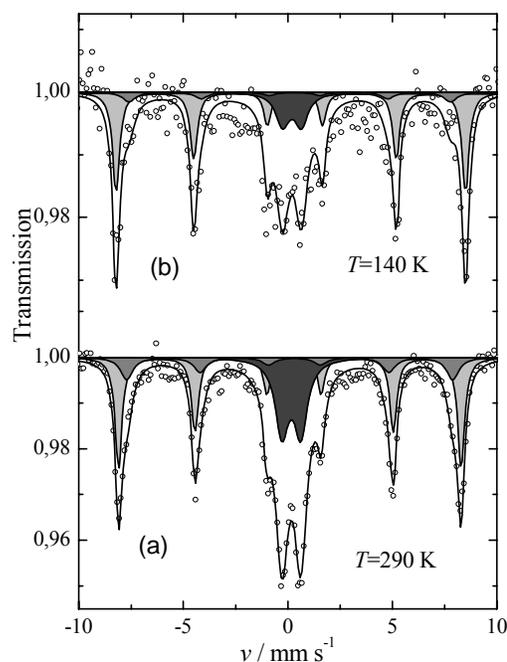


Figure 6: Mössbauer spectra at 290 K (a) and 110 K (b) temperatures of the film material fabricated by iron anodizing in the DMSO electrolyte after annealing at 500 °C for 3 h using 1 °C/min ramping.

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