



Title	Ex Situ Evidence for the Role of a Fluoride-Rich Layer Switching the Growth of Nanopores to Nanotubes: A Missing Piece of the Anodizing Puzzle
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A missing piece of anodizing puzzle: *ex-situ* evidence on the role of fluoride-rich-layer switching the growth of nanopores to nanotubes

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Abstract: Anodizing is a high voltage electrochemical conversion process that forms barrier-type oxide layers or self-organized nanoporous/nanotubular structures. So far, the Al_2O_3 -like nanopores and TiO_2 -like nanotubes could be successfully synthesized on many metals and alloys. The proposed models of anodic oxide nanotubes growth, however, sacrifice from lack of evidence on the transition from nanopores to nanotubes. The present study demonstrates a missing piece of this anodizing puzzle which is responsible for the formation of nanotubes in fluoride-containing organic electrolytes. For this purpose, we choose an anodic oxide formed on iron, as a model case, because both nanotubes and nanopores can be formed and slow kinetics of transition between those two forms allows us to observe *ex-situ* a fluoride-rich-layer upon nanopores/nanotubes transition. The compositional fingerprints of this transition shed a light on the general mechanism of nanotubes growth in fluoride-containing electrolytes.

Introduction

Anodizing of valve metals and alloys typically leads to formation of a barrier-type anodic oxide layer^[1] or an oxide of porous nature which is organized in the form of nanopores/nanotubes^[2] at strictly defined electrochemical conditions. The formation of self-organized nanopores/nanotubes on Al,^[2a] Ti,^[3] Zr,^[4] and other valve metals has attracted scientific and technological interests over the last decade. Interestingly, some metals such as Al,^[2a] Nb,^[5] and Ta^[6] tend to produce porous structures (Al_2O_3 -like), while others such as Ti,^[3] Zr,^[4] and Hf^[7] produce nanotubular structures (TiO_2 -like). Recently, the formation of self-organized oxide nanopores/nanotubes has been extended to iron and stainless steel.^[8] The anodizing of iron is more challenging issue in view of its corrosion in aqueous electrolytes.^[9] The key for formation of nanotubes and nanopores is, therefore, a good control over the iron

corrosion/passivity which can be effectively achieved in organic electrolytes containing a small amount of water and fluorides.^[8d, 8e]

The essential difference between nanostructures formed on aluminum (Al_2O_3 -like) and titanium (TiO_2 -like) is the gap between pores which forms the shape of pores for Al_2O_3 or nanotubes for TiO_2 . It is generally recognized that the gap in between nanotubes is associated with migration of fluoride ions incorporated from fluoride-containing electrolytes into anodic films during the anodizing process. Although the behavior of fluoride ions during the formation of anodic nanopores/nanotubes is not well understood, it is known that during anodizing of Ti, Al and Ta the inward mobility of F^- is approximately twice that of O^{2-} ions, leading to formation of a thin fluoride-rich-layer at the metal/film interface.^[10] So far, the formation of fluoride-rich-layer was evidenced for barrier-type anodic oxide formed on Ti by means of glow discharge optical emission spectroscopy (GDOES) depth profiling method.^[10b] Its formation is an effect of simultaneous migration of anions present in the electrolyte towards the metal/oxide interface together with migration of cations towards the opposite direction under the influence of electric field strength of $\sim 10^8 \text{ V m}^{-1}$.

The transition from the barrier-type layer to the nanopore/nanotube is associated with whether a film material is formed at the film/electrolyte interface.^[11] The barrier-type layer of amorphous anodic oxides generally form both at the metal/film and film/electrolyte interfaces by simultaneous migration of anions inwards and cations outwards, respectively, under the high electric field. The nanopores/nanotubes of anodic oxides are developed when no film material is formed at the film/electrolyte interface and outwardly migrating cations are directly ejected into electrolyte. In this particular case, film growth proceeds only at the metal/film interface. Because of faster migration of F^- ions relative to O^{2-} ions, as discussed above, a thin fluoride-rich layer is formed adjacent to the substrate. Simultaneous flow of film material from pore base to pore wall by field-assisted plastic flow^[12] extends the fluoride-rich layer to the cell boundaries of the porous layer. Because of solubility of fluoride-rich-layer in electrolyte during the anodizing process, the native porous character is presumed to be turned into nanotubular one. After transition of nanopore to nanotube, the size of space in between nanotubes would be approximately equal to double thickness of fluoride-rich-layer.

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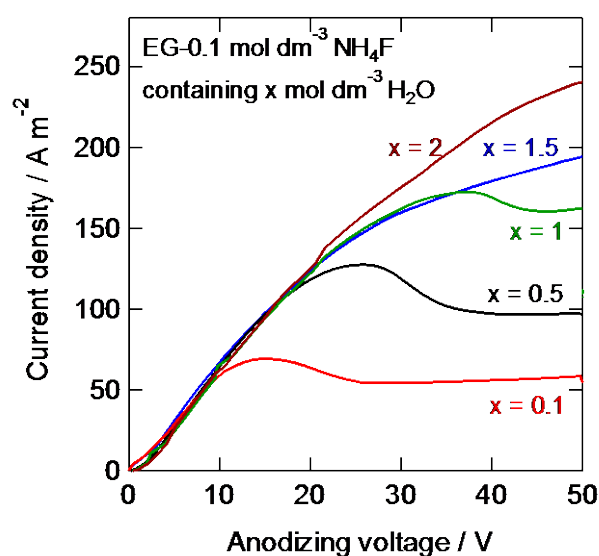
Such scenario seems to be valid for many anodic oxides formed in fluoride-containing electrolytes, in which the formed metal-fluoride-complex is dissolved during anodizing process. By looking at the literature data, some reports explain the anodic nanotubes growth by means of a fluoride-rich-layer present in between nanotubes,^[13] but, except the schemes little scientific evidence has been given. The difficulty in detection of the layer is possibly caused by its nano-size and fast dissolution kinetics, and so far there was no *in-situ* and *ex-situ* confirmation on its role in the shaping of anodic oxide into nanotubes.

In the present study, the presence of fluoride-rich-layer in the formation of nanotubes/nanopores has been directly imaged for the first time using high resolution transmission electron microscopy/EDS elemental mapping. Herein, we established the anodizing process at the electrochemical conditions in which the transition of nanopores to nanotubes is possible, well controllable, and therefore allows us to detect *ex-situ* the formed fluoride-rich-layer. To make it possible, FIB cross-section anodic nanotubular/nanoporous slides were observed by transmission electron microscope equipped with high sensitivity EDS detector allowing elemental mapping at the nanoscale resolution. The presented compositional fingerprints are an evidence on the role of fluoride-rich-layer in the formation of anodic nanotubes on iron. However, the general mechanism presented here may explain formation of anodic oxides such as: TiO_2 , ZrO_2 , HfO_2 , etc.

Results and Discussion

Influence of water concentration

In anodizing of metals to form nanoporous/nanotubular oxide films in organic electrolytes the water concentration in the electrolytes play an important role in growth rate, morphology and phase of the developed anodic films.^[8d, 14] Here we examined the influence of water concentration on the growth behavior of the porous anodic films on iron to get insight into the growth mechanism of the nanoporous/nanotubular films. Figure 1 shows the potentiodynamic *i*-*V* curves of iron during anodizing to 50 V at a sweep rate of 1.0 V s^{-1} in ethylene glycol (EG) electrolyte containing 0.1 mol dm^{-3} ammonium fluoride and various concentrations ($0.1 - 2 \text{ mol dm}^{-3}$) of water. At the lowest water concentration of 0.1 mol dm^{-3} , a current maximum appears at 14 V, followed by a gradual current decrease up to 25 V, above which a steady-state current of 55 A m^{-2} is observed. The maximum current in addition to the voltage of current maximum increases with an increase in the water concentration. At water concentrations of $>1.0 \text{ mol dm}^{-3}$, no current maximum appears and the current increases continuously with anodizing voltage. It is interesting that the current density during initial linear voltage rise in the low voltage region is not dependent upon the water concentration. In contrast, the current density at 50 V increases with an increase in the water concentration, from ~ 55 to $\sim 240 \text{ A m}^{-2}$. It is known that a barrier-type anodic film is developed at the initial period of anodizing of aluminum in acid electrolytes prior to the initiation of pores.^[15] Figure 1 suggests that the growth of



initial barrier layer is not largely influenced by water concentration,

Figure 1. Potentiodynamic *i*-*V* curves of iron during anodizing to 50 V at 1 V s^{-1} in EG electrolyte containing 0.1 mol dm^{-3} ammonium fluoride and $x \text{ mol dm}^{-3}$ water at 293 K.

but the growth of the porous layer is highly influenced by the water concentration in electrolyte. In subsequent potentiostatic anodizing at 50 V (Figure S1) the current density gradually changes to a steady-state value after reaching to 50 V at all water concentrations. The steady-state current density also increases with an increase in water concentration.

Figure 2 shows the film thickness and electric charge passed during anodizing potentiodynamically and then potentiostatically at 50 V for 900 s at various water concentrations. The electric charge increases linearly with water concentration. As a consequence of this increase in the electric charge during anodizing, the thickness of the anodic film also increases with water concentration up to 1.5 mol dm^{-3} water. However, at 2.0 mol dm^{-3} water the thickness of the anodic film remarkably reduced even though the electric charge is further increased. The reduced film thickness may be associated with enhanced chemical dissolution and gas evolution during anodizing at the high water concentration. The enhanced gas generation during anodizing at 50 V with an increase in the water concentration is clearly seen in Figure S2. On the surface of the specimens, which are located at the top-left side of each photo, the number and size of gas bubbles on the specimen surface increase with water concentration. Despite the increased gas generation efficiency with water concentration, the film thickness increases along with the increased electric charge except for 2.0 mol dm^{-3} water, suggesting that an additional factor increasing the film thickness under the increased gas generation efficiency (reduced film formation efficiency) appears to exist at higher water concentrations (a transition of growth mechanism from field-assisted dissolution to field-assisted flow, as discussed layer).

The surfaces and cross-sections of the anodized specimens at various water concentrations were examined by scanning electron microscopy (Figure 3). A porous anodic film is developed

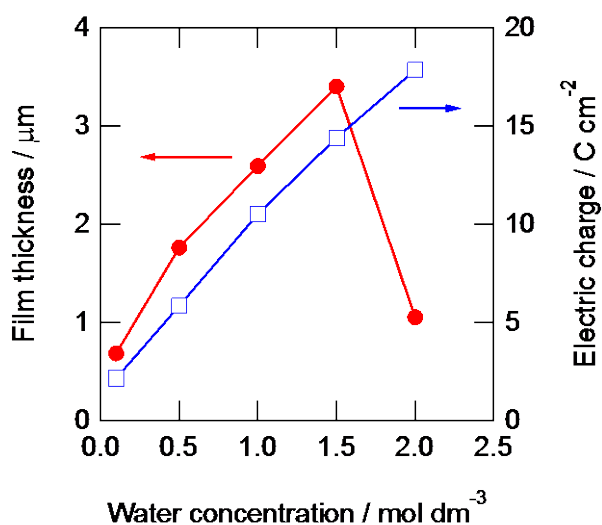


Figure 2. Film thickness and electric charge passed during anodizing potentiodynamically to and following potentiostatically at 50 V for 900 s in the EG electrolyte containing 0.1 mol dm⁻³ ammonium fluoride and water at 293 K as a function of water concentration.

even at the lowest water concentration of 0.1 mol dm⁻³ (Figure 3a), but the pore size is rather small and some cylindrical pores are not clearly seen in the cross-section image (Figure 3e). The thickness of the anodic film is 0.68 μm and that of the barrier layer, located between the outer porous layer and iron substrate, is 120 nm. When the water concentration is increased, cylindrical pore channels, which are normal to the metal/film interface, are more clearly seen in both surface and cross-section scanning electron micrographs. Many pores penetrate from the film surface to the barrier layer. The pore size observed at the film surface appears to increase with water concentration. Because of increased chemical dissolution at 2.0 mol dm⁻³ water, the surface and outer part of the anodic films become rough and irregular, as seen in Figures 3d and 3h. The thickness of the barrier layer decreases from 120 nm at 0.1 mol dm⁻³ water to 60 nm at 2.0 mol dm⁻³ water (Figure S3). The interpore distance of nanoporous anodic alumina films formed in aqueous acid electrolytes increases linearly with thickening of the barrier layer,^[16] but in this study, the interpore distance tends to increase with an increase in water concentration despite the reduction of barrier layer thickness (Figure S3).

Another important feature is the morphology of the metal/film interface. It is well known that porous anodic alumina films developed in aqueous acid electrolytes, such as sulfuric acid, oxalic acid, and phosphoric acid, show scalloped metal/film interface, and the film morphology is described by a Keller-Hunter-Robinson model.^[17] Similar scalloped interface is developed when the water concentration in the electrolyte is

relatively high (1.5 and 2.0 mol dm⁻³) as shown in Figure 4a, but the interface is rather flat at the lower water concentrations (Figure 4b). These findings suggest the change in growth mechanism with water concentration in electrolyte, as discussed later in detail.

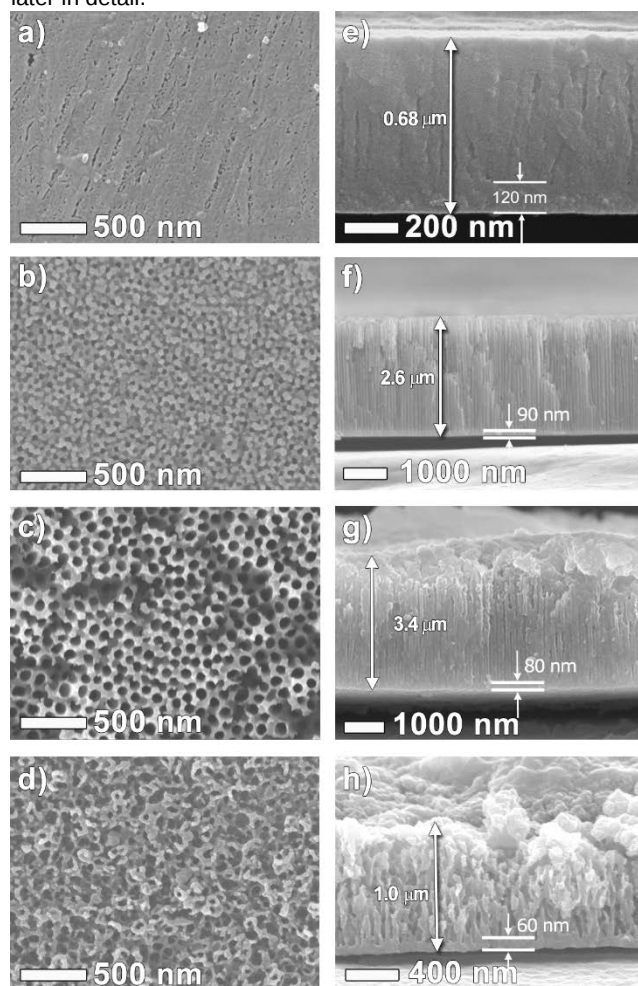
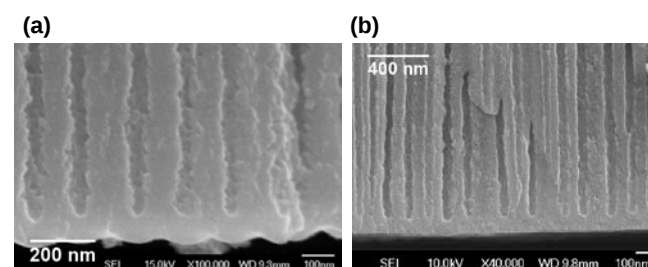


Figure 3. Scanning electron micrographs of (a-d) surfaces and (e-h) cross-sections of iron anodized at 50 V for 900 s in EG electrolytes containing 0.1 mol dm⁻³ ammonium fluoride and (a,



e) 0.1, (b, f) 1.0, (c, g) 1.5, (d, h) 2.0 mol dm⁻³ water at 293 K.

Figure 4. Scanning electron micrographs of cross-sections of the bottom of the anodic films formed by anodizing of iron at 50 V for 900 s in EG electrolytes containing 0.1 mol dm⁻³

ammonium fluoride and (a) 1.5 and (b) 1.0 mol dm⁻³ water at 293 K.

The change in the barrier layer thickness and the film and interface morphologies with water concentration may be associated with compositional change of the anodic films. Therefore, we examined the composition of anodic films formed at various water concentrations qualitatively by GDOES elemental depth profile analysis. Examples of the anodic films formed at 0.1 and 1.5 mol dm⁻³ water concentrations are shown in Figure 5, in which the intensity ratio of carbon, oxygen, and fluorine to iron was plotted as a function of sputtering time. The anodic films contain fluorine, carbon and oxygen species, derived from fluoride, EG and water/EG in electrolyte, respectively, in addition to iron. Obviously, the intensity ratios of carbon, oxygen and fluorine to iron are all higher at 0.1 mol dm⁻³ water compared with at 1.5 mol dm⁻³ water. The excess amounts of electrolyte species are incorporated in the anodic films formed at lower water concentrations, probably influencing the field strength of the barrier layer in the growing anodic films. As a consequence, the thickness of the barrier layer changes with water concentration. In Figure 5 a steep intensity reduction for fluorine, oxygen and carbon at sputtering time of 13 s, and 35 s at water concentrations of 0.1 and 1.5 mol dm⁻³, respectively, indicates the location of the metal/film interface. The sputtering time to the metal/film interface is shorter for the anodic film formed at 0.1 mol dm⁻³ water compared with at 1.5 mol dm⁻³ water, in agreement with the thinner film formation at lower water concentration.

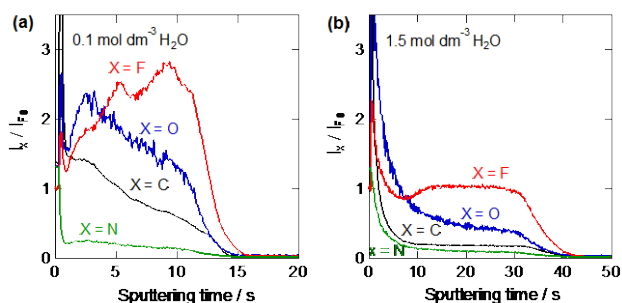


Figure 5. GDOES elemental depth profiles of the anodic films formed by anodizing of iron at 50 V for 900 s in EG electrolytes containing 0.1 mol dm⁻³ ammonium fluoride and (a) 0.1 and (b) 1.5 mol dm⁻³ water at 293 K.

Influence of formation voltage

The anodic films formed on iron at 50 V were nanoporous regardless of water concentration in electrolyte (Figure 3). It was reported that iron oxide nanotube arrays were formed at higher anodizing voltages.^[18] Thus, we next examined the influence of formation voltage on the film morphology. Figure S4 shows the current-time curves for anodizing of iron at formation voltages from 30 to 100 V at the water concentration of 1.5 mol dm⁻³. Current density increases continuously during initial potentiodynamic anodizing at a sweep rate of 1 V s⁻¹. In the following potentiostatic step for 900 s, the current density

becomes almost constant at the formation voltages between 30 and 60 V. At higher voltages of >60 V the current density increases continuously with a slope increasing with formation voltage due to the Joule heating effect. This is evident from Figure S5 where the variation of the electrolyte temperature with anodizing time at 40 and 100 V is demonstrated. The electrolyte surface temperature was monitored using an infrared thermometer. Although the thermometer was not well calibrated, it is obvious that the electrolyte temperature rose gradually during anodizing at 100 V while a constant temperature was maintained at 40 V. Thus, the continuous current rise at voltages higher than 60 V (Figure S4) appears to be associated with the rise of the electrolyte temperature.

Figure 6 shows the surface morphology of anodic films formed at various formation voltages. The anodic films developed at voltages from 30 to 50 V are nanoporous with the Al₂O₃-like geometrical structure.^[2a] The pore size increases with anodizing voltage as expected for many nanoporous/nanotubular structures formed by anodizing of valve metals. The transition of nanopores to nanotubes is observed for specimens anodized at increased voltages of 60 to 100 V.

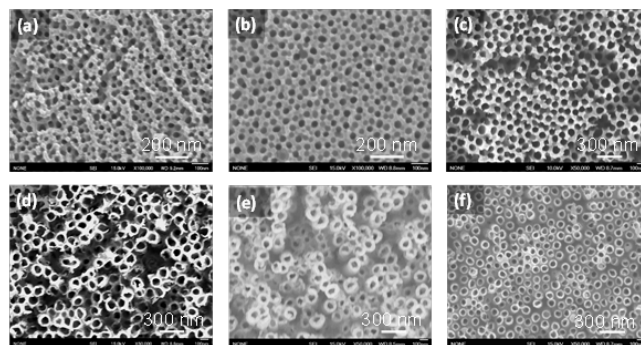


Figure 6. Scanning electron micrographs of the anodic films formed on bulk iron sheet at the selected voltages of (a) 30 V, (b) 40 V, (c) 50 V, (d) 60 V, (e) 70 V and (f) 100 V for 900 s in the ethylene glycol electrolyte containing 1.5 mol dm⁻³ water and 0.1 mol dm⁻³ ammonium fluoride at 293 K.

Cylindrical pores/nanotubes aligned perpendicularly to the metal/film interface are evident from cross-section images in Figure 7. The close inspection of the cross-sections (60–100 V) reveals that upper part of oxide is composed of nanotubes and the bottom part is composed of nanopores. A ratio between fractions of nanotubes and nanopores strongly depends on applied voltage as demonstrated in Figures 7b and 7c. The total thickness of anodic film increases with anodizing voltage up to 70 V from 2.7 μm at 40 V to 3.6 μm at 70 V, because of the rise of electric charge. The film thickness is reduced to ~3 μm at 100 V, even though the electric charge is remarkably increased. The rise of the electrolyte temperature (Figure S5) at this high formation voltage probably enhanced chemical dissolution of the anodic film, contributing at least partly to the reduction of film thickness. A rapid gas evolution, which was observed with the naked eye at the high anodizing voltage of 100 V (less significant at lower voltages), was also likely to contribute to the thickness reduction, in addition to the faster film dissolution.

The formation voltage was also changed by galvanostatic anodizing of iron at various current densities (Figure S6). Higher current densities lead to higher anodizing voltages. At the commencement of galvanostatic anodizing a voltage surge appears.

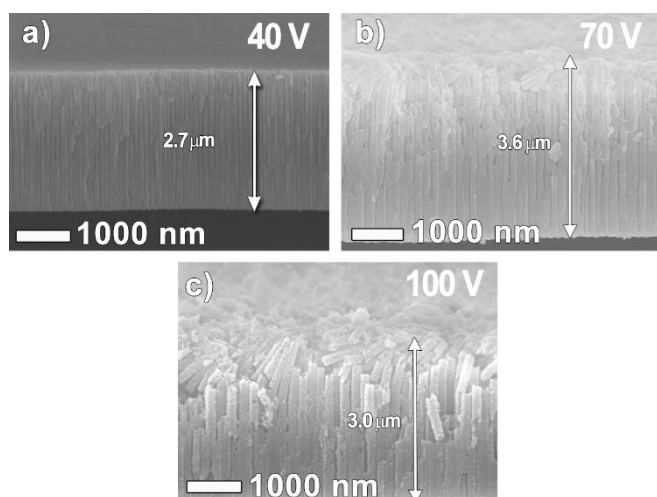


Figure 7. Scanning electron micrographs of the cross-sections of anodic films formed on bulk iron sheet at a sweep rate of 1 V s^{-1} in the ethylene glycol electrolyte containing 1.5 mol dm^{-3} water and 0.1 mol dm^{-3} ammonium fluoride (a) 40 V, (b) 70 V, and (c) 100 V at 293 K.

The surge voltage increases from $\sim 10 \text{ V}$ at 100 A m^{-2} to $\sim 120 \text{ V}$ at 1500 A m^{-2} . Such a large voltage surge is mainly related to the high ohmic resistance of the electrolyte employed. Then, the voltage increases approximately linearly with time to a plateau voltage, which also increases with the applied current density. The plateau is then followed by sharp voltage decline, reaching a steady-state voltage. The steady-state voltage increases largely with applied current density up to 750 A m^{-2} . No further rise of the anodizing voltage is found above 750 A m^{-2} , probably because of the rise of the electrolyte temperature at high current densities, as shown in Figure S5.

The transition from nanopores to nanotubes was also found at high voltages of $>70 \text{ V}$ at steady-state conditions (Figure S7). Nanoporous films are obtained at $\leq 500 \text{ A m}^{-2}$, where the steady-state formation voltage is $<70 \text{ V}$ (Figures S7a–7c). Above 500 A m^{-2} , nanotubular morphology is observed (Figures 7d–7f). Taking into account the voltage response in Figure S6, nanopores and nanotubes were formed below and above the critical voltage of 70 V , respectively, which is more or less in agreement with potentiostatic anodizing.

Distribution of fluoride in the anodic films

Potentiostatic anodizing discloses that nanoporous films are formed at low formation voltages, while the film structure is transformed into nanotubes at high anodizing voltages (Figure 6). It is well known that anodic nanotubes are formed on titanium in electrolytes containing fluorides and it is generally expected that nanotubular shape is formed by preferential dissolution of the fluoride enriched cell boundaries.^[13] However, the fluoride-enriched layer has not been directly observed so far either by *in-situ* or *ex-situ* observations. The atomic resolution analytical electron microscope was employed to get further insight of the origin of tubes formation on iron, as a model case, by exploring

the fluoride distribution in the anodic films at the nanometer scale. For this purpose, two anodizing specimens, one with nanoporous structure formed at low voltage (1 V s^{-1} , 40 V) and other with nanotubular structure formed at high voltage (1 V s^{-1} , 100 V) were investigated.

Figure 8 displays the bright field (BF) images and corresponding EDS maps for the specimens formed at 100 V, which reveal the fluorine, oxygen, and iron at the bottom, middle, and top regions of anodic oxides. Fluoride enrichment at the cell boundaries which construct the outer shell of nanotube/nanopore can be clearly seen in these images. Assuming faster migration of fluoride species compared with oxide ions, the film formed at metal/oxide interface should consist of iron fluoride and that formed at oxide/electrolyte interface containing fluorine species, oxygen, and iron, forming the outer-shell and the inner-shell of nanopore/nanotube, respectively.^[10b] Scalloped metal/film interface can be clearly seen from these EDS/BF images (Figure 8a). It is obvious that fluoride-enriched-layer of uniform thickness is present at the metal/film interface and in between nanotubes/nanopores. However, the outer-shell of nanotube/nanopore taken from the top of anodic oxide (Figure 8c) appears to be depleted in fluorine because of accelerated etching of this region. This is more obvious in the superimposed EDS mapping of oxygen and fluorine, indicating that nanotubes are formed by the preferential dissolution of the fluoride-rich-layer (brown color) at the top part of the anodic film. Since the top part of the oxide is formed during early stage of anodizing and is exposed to the electrolyte for a longer period of time, it is likely that preferential dissolution of the fluoride-rich-layer is only limited to the top of oxide, thus forming the nanotubes in the outer part of the anodic film at 100 V.

BF and EDS images of FIB cross-section of the anodic film formed at 40 V in the same electrolyte are presented in Figure 9. These images reveal that fluoride-rich shells in between nanotubes/nanopores are also formed at 40 V. The fluoride-rich shell of nanopore/nanotube is the most obvious for EDS mapping taken from the bottom and middle part of nanostructure, but at the top part of the film (Figure 9c), particularly in the upper region in this image, the fluoride-rich shell is less obvious in EDS images, and fluorine and oxygen are more uniformly distributed in the outermost film region. Therefore, no preferential dissolution of cell boundaries occurs and the nanoporous structure instead of the nanotubes is developed at 40 V. The chemical dissolution of the porous layer usually occurs during anodizing to form a nanoporous/nanotubular anodic film. If the outer part of the anodic film formed at 40 V is chemically dissolved, the fluoride-enriched cell boundaries will be exposed to electrolyte, leading to the preferential dissolution of cell boundaries and development of nanotube morphology. This was confirmed by prolonged anodizing at galvanostatic anodizing at 300 A m^{-2} with a steady-state formation voltage of $\sim 50 \text{ V}$. After anodizing for 900 s the surface scanning electron micrograph shows a nanoporous morphology (Figure 10a), which transforms to nanotubular after anodizing for 1800 s (Figure 10b). The interpore distance increases clearly after prolonged anodizing,

as is evident in Figure 10, suggesting the chemical dissolution of initially formed outer

containing 1.5 mol dm^{-3} water and 0.1 mol dm^{-3} ammonium fluoride at 293 K.

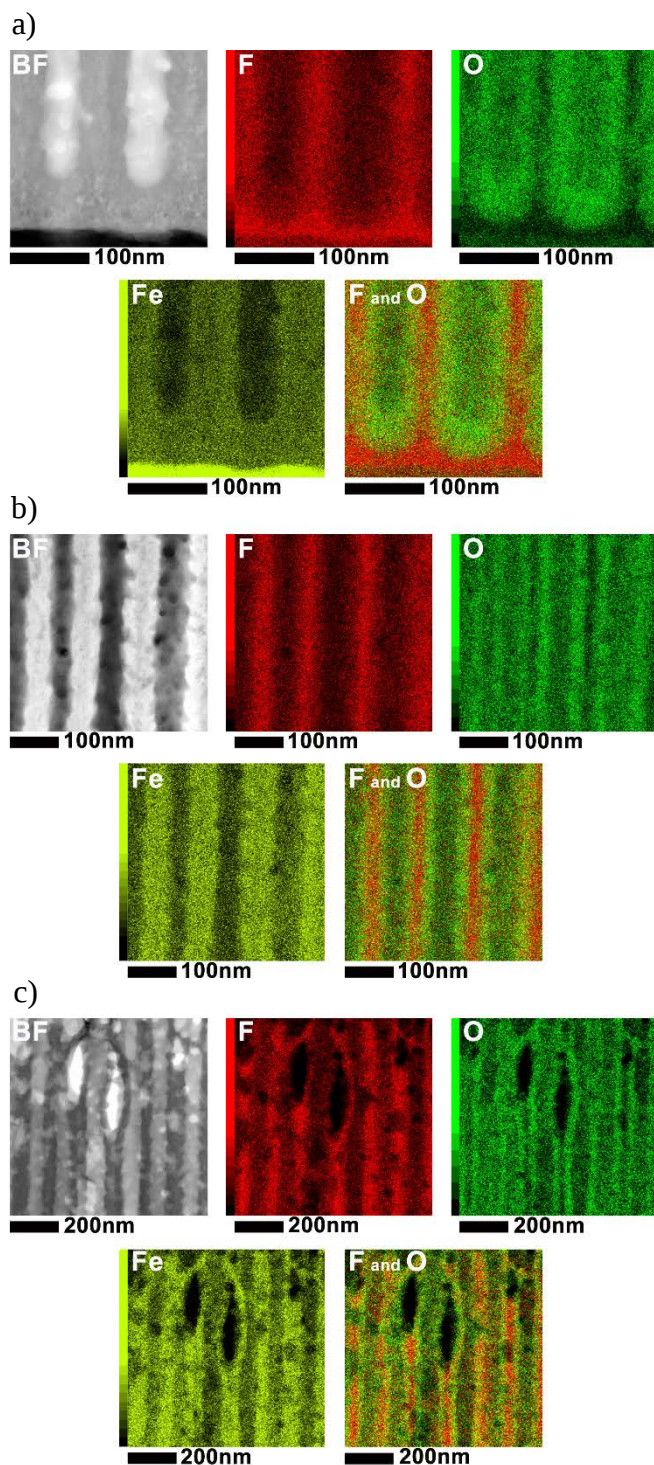


Figure 8. Bright field images and corresponding EDS maps of (a) bottom, (b) middle, and (c) top regions of FIB-treated anodic film formed on iron at 100 V in the ethylene glycol electrolyte

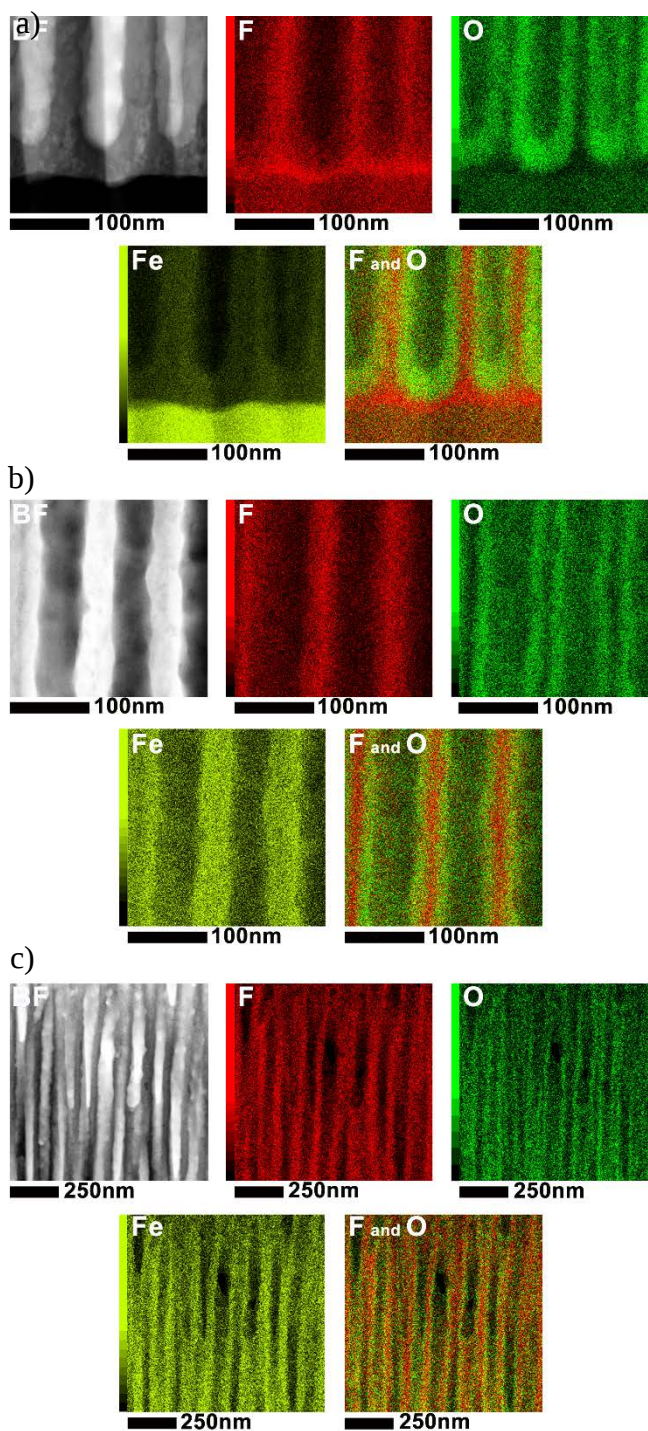


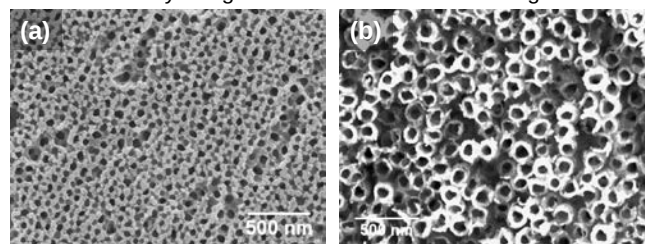
Figure 9. Bright field images and EDS maps of (a) bottom, (b) middle, and (c) top regions of FIB-treated anodic film formed on

iron at 40 V in the ethylene glycol electrolyte containing 1.5 mol dm⁻³ water and 0.1 mol dm⁻³ ammonium fluoride at 293 K.

layer with rather uniform oxygen and fluorine distribution to expose the later-developed inner layer with clear fluoride-enriched cell boundaries to electrolyte. The present work shows the formation of iron-based nanoporous and nanotubular anodic oxides in fluoride-containing organic electrolytes and clearly reveals the presence of fluoride-rich-layer at the cell boundaries of porous structure for the first time. The direct evidence of fluoride-rich-layer and dissolution of such layer in between nanopores/nanotubes at the top of nanostructure indicates that fluoride-rich-layer is the key reason for the transition from nanopores to nanotubes. The exact chemical structure of fluoride-rich-layer is unknown in the present study. However, a previous RBS study of a thin barrier film formed on iron by potentiodynamic anodizing in the similar electrolyte disclosed that the inner layer was composed of oxygen-free FeF₃.^[19] Since the outer layer contained oxygen species, the inner layer was formed as a consequence of the faster migration of fluoride ions relative to the oxygen species. Thus, even in the present nanoporous/nanotubular anodic films, it is likely that the composition of fluoride-rich-layer would be oxygen-free FeF_x (FeF₂, FeF₃, or similar). The question which arises here is, of course, if the fluoride-rich-layer is soluble in immersed electrolyte or electric field is necessary to dissolve the layer. Both compounds of FeF₂ and FeF₃ are insoluble in organic solvents, freely soluble in HF, and slightly soluble in water with 8.3×10^{-3} mol dm⁻³ and 5.2×10^{-1} mol dm⁻³ for FeF₂ and FeF₃, respectively.^[20] The presence of nanopores instead of nanotubes at lower voltages/currents reveals that the chemical dissolution kinetics of initially formed film material with relatively uniform elemental distribution of fluorine and oxygen is rather slow. The influence of the field-aided-dissolution of fluoride-rich-layer can be negligible from the morphological point of view. The transition depth from the outer nanotube to inner nanopores is far from the barrier layer as seen in Figure 7. The electric field is mainly applied in the barrier layer. Thus, the preferential chemical dissolution of the oxygen-free, fluoride-enriched layer at the cell boundaries relative to the outer shell consisting probably of iron oxyfluoride is a critical factor for shaping into nanotubes. Since fluoride-enriched cell boundaries are formed both at 40 V and 100 V, and a nanoporous-to-nanotube transition occurs even at relatively low voltage (~50 V) after prolonged anodizing (Figure 10). Thus, the formation voltage is not a critical factor for the transition. The fluoride-enriched cell boundaries are not developed from the beginning of anodizing; fluorine and oxygen species are rather uniformly distributed in the initially formed film. It is most likely from the present study that the nanotubular morphology is developed after chemical dissolution of the initially formed film and exposure of the fluoride-enriched cell boundaries to electrolyte. At high formation voltages the electrolyte temperature rises (Figure S5), contributing the accelerated chemical dissolution and nanotube formation. Thus, higher formation voltage and higher electrolyte

temperature are preferable for the formation of nanotubular anodic films on iron more rapidly.

The fluoride-enriched cell boundaries were found at 1.5 mol dm⁻³ water in electrolyte regardless of the formation voltage. However,



the distribution of fluoride in anodic films changes with the water concentration.

Figure 10. Scanning electron micrographs of the anodic films formed on iron at 300 A m⁻² for (a) 900 s and (b) 1800 s in EG electrolyte containing 1.5 mol dm⁻³ H₂O and 0.1 mol dm⁻³ ammonium fluoride at 293 K.

Figure 11 shows the BF images and corresponding EDS map of the anodic film formed at 50 V in EG electrolyte containing a low concentration (0.1 mol dm⁻³) of water. The anodic film is 860 nm thick (Figure 11a) with a relatively thick barrier layer. The metal/film interface is relatively smooth and not scalloped. The distance from the metal/film interface to the pore base is as large as ~290 nm (Figure 11b). From the corresponding EDS map, a thick fluoride-enriched layer of 120 nm thickness (orange color) is seen clearly next to the iron substrate (Figure 11c). The fluoride-enriched layer in this anodic film is extremely thicker than those formed at high (1.5 mol dm⁻³) water concentration and 40 and 100 V (Figures 8 and 9). Above the fluoride-enriched layer an oxygen-containing barrier layer is present with its composition being similar to that of a porous layer above the barrier layer. The fluoride distribution is rather uniform in the porous layer and no fluoride-enriched cell boundaries are present in this anodic film. The absence of the fluoride-enriched cell boundaries should be a main reason for the formation of nanoporous anodic films at lower water concentrations.

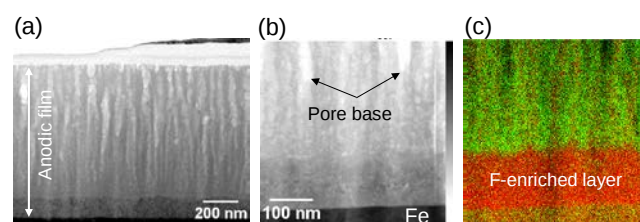


Figure 11. Bright field and corresponding EDS images of the FIB cross-section of the anodic film formed on iron at 50 V in EG electrolyte containing 0.1 mol dm⁻³ ammonium fluoride and 0.1 mol dm⁻³ water at 293 K. The fluorine and oxygen distributions (c) are indicated as orange and green colors, respectively.

Growth mechanism

Schematic illustrations of the film morphologies formed at low and high water concentrations are demonstrated in Figure 12. At

the low water concentration (Figure 12a), a barrier layer adjacent to the iron substrate is thick and the metal/film interface is flat, being unusual for porous film growth. The film morphology similar to nanoporous Al_2O_3 and nanotubular TiO_2 films is formed at the high water concentration (Figure 12b): scalloped metal/film interface and relatively thin barrier layer.

Two major growth mechanisms have been proposed for formation of porous anodic alumina films: classical field-assisted dissolution^[21] and recently proposed field-assisted flow.^[12] During porous alumina growth, the thickness of barrier layer between the aluminum substrate and the porous outer layer is kept constant under a constant formation voltage. In the field-assisted dissolution model, film growth proceeds at the metal/film interface by inward migration of O^{2-} ions, whereas the outwardly migrating Al^{3+} ions are directly ejected to electrolyte at pore base, at which enhanced dissolution of film occurs under the high electric field, with a balance between the growth and dissolution of the film maintaining a constant thickness of the barrier layer in steady-state growth. Flow of film material from pore base to pore wall was proposed from a tungsten tracer study in film growth in phosphoric acid.^[12a] The flow is caused by stress generated in the growing barrier layer.^[12c, 22] The tracer studies suggested that the flow model is applicable to the porous alumina growth in sulfuric acid, oxalic acid malonic acid and phosphoric acid,^[12a, 22b, 23] whereas field-assisted dissolution is predominant in chromic acid and alkaline borax electrolytes.^[24] In the former four electrolytes, alumina films incorporated with electrolyte anions are formed. In contrast, relatively pure alumina practically free from electrolyte anion species is developed in the latter two electrolytes. Therefore, film composition plays a key role in the growth mechanism, probably because the film composition changes the mechanical properties of alumina films.

The growth mechanism of the present anodic films formed on iron may be dependent upon the water concentration in electrolyte, because the film composition changes with the water concentration (Figure 5). In the anodic film formed at the low water concentration, it is unlikely that the field-assisted flow occurs from the morphological point of view: rather thick barrier layer compared with the interpore distance (Figure 11) and the flat metal/film interface. Under the absence of flow, fluoride-enriched layer thickens as a consequence of the faster migration of fluoride ions relative to oxygen species. At the high water concentration, flow of film material from the pore base to pore wall is expected from the thin barrier layer that is smaller than the interpore distance and the scalloped metal/film interface. The thinner fluoride-enriched layer adjacent to the iron substrate is another evidence of the displacement of the fluoride-enriched layer from the pore base to pore wall and as a consequence, the fluoride-enriched layer extends to the cell boundaries in the porous layer.

Conclusions

The present study shows, for the first time, an *ex-situ* evidence on the role of fluoride-rich-layer in the growth of

nanoporous/nanotubular anodic oxide formed on iron in ethylene glycol electrolyte containing 0.1 mol dm^{-3} ammonium fluoride (NH_4F) and various concentrations of water. Based on the results obtained in the present study, the following conclusions can be drawn:

- The transition between nanopores and nanotubes is evident at high water concentration (1.5 mol dm^{-3}) from transmission electron microscopy observations supported by high resolution EDS mapping.
- The space in between iron nanotubes is formed by fluoride-rich-layer (FeF_x) which is dissolved preferentially in electrolyte during the anodizing process. The dissolution of FeF_x is accelerated at enhanced voltages/currents due to rise of electrolyte temperature.
- Nanopores are nanotubes; the compositional fingerprints for iron oxide formed at 40 V and 1.5 mol dm^{-3} water reveal the shape of iron oxide nanotubes beneath nanoporous structure. So called, nanopores observed on SEM images are composed of iron oxide nanotubes, separated by a FeF_x thin layer.
- Water content in electrolyte has a beneficial role on the growth mechanism of anodic oxide on iron. At low water concentrations anodic oxide growth is in line with the classical field-assisted dissolution model, whereas high water concentrations lead to the field-assisted flow model.

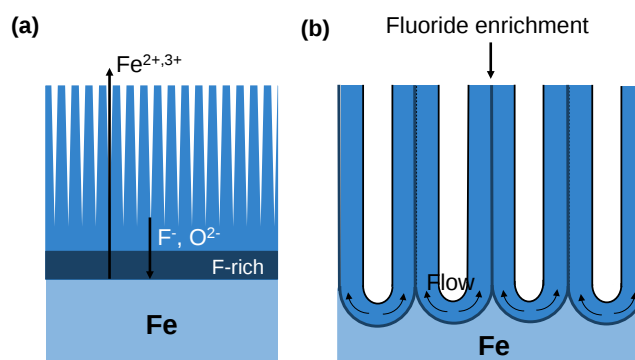


Figure 12. Schematic illustrations of the film morphology and growth mechanism of the nanoporous anodic films on iron at (a) low and (b) high water concentrations.

Experimental Section

High purity iron sheet (99.99 %, Nilaco Corporation, Japan) of thickness of 0.3 mm was used as a substrate after mechanical polishing using 1500 grit SIC paper followed by polishing using Al_2O_3 abrasives of $3 \mu\text{m}$ diameter and ultrasonically degreased in acetone. Anodic films on iron were formed either by potentiodynamic anodizing (1 V s^{-1}) to the selected voltage or galvanostatically at selected current density in 100 cm^3 ethylene glycol (EG) electrolyte containing 0.1 mol dm^{-3} ammonium fluoride (NH_4F) and 1.5 mol dm^{-3} of water. Anodizing was carried out in two electrode system with a platinum sheet as a cathode and iron specimen as an anode. The distance between working and counter electrode was kept constant at 20 mm. The anodizing bath was placed in the thermostated water bath controlled at 293 K using a SCINICS multi-

thermal unit CH-1501, while the temperature of electrolyte surface was monitored by a SATO SK-8300 infrared thermometer. After anodizing, the specimens were ultrasonically washed in ethylene glycol, followed by rinsing in acetone and then dried in an air stream. Surface morphology and cross-sections of anodic films were examined by JEOL JSM 6500F field emission scanning electron microscope operated at an accelerating voltage of 15 kV. Fluoride enrichment study of nanoporous and nanotubular anodic films formed on iron at various water concentrations was examined by JEOL, JEM-ARF-200F atomic resolution analytical electron microscope. The machine is used owing to its unprecedented high resolution for the detection of light elements. Prior to fluoride enrichment study, electron-transparent sections were prepared by a Hitachi FB-2 2100 FIB system employing a Ga⁺ ion beam. The resistance of 1.5 mol dm⁻³ ethylene glycol electrolyte containing 0.1 mol dm⁻³ NH₄F was determined by Electrochemical Impedance Spectroscopy (IVIUM Technology Compact Stat Interface) using an AC amplitude of 10 mV, in a frequency range 10⁵–10⁻¹ Hz in a two electrode system employing platinum foils as a working and counter electrodes.

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Keywords: anodizing • iron oxide nanotubes • anodic oxide • fluoride-rich-layer

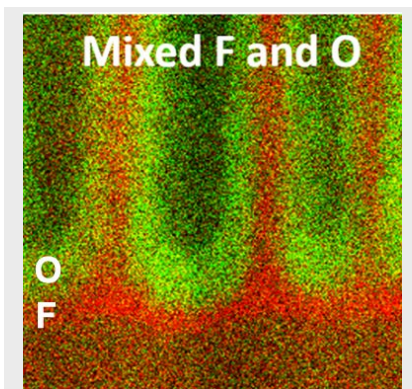
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

ARTICLE

Nanotubes or nanopores? The reason for formation of anodic nanotubes such as TiO_2 and Fe_xO_y has remained unclear so far. Herein, for the first time the presence of fluoride-rich-layer (red color) responsible for shaping of nanopores into nanotubes has been directly imaged using high resolution TEM/EDS elemental mapping.



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Chunyu Zhu, Yoshitaka Aoki, and Hiroki
Habazaki,*

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**A missing piece of anodizing puzzle:
ex-situ evidence on the role of
fluoride-rich-layer switching the
growth of nanopores to nanotubes**