Combinatorial electrochemistry on Al–Fe alloys

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Abstract
Combinatorial material development was combined with high throughput microelectrochemistry to allow an efficient but comprehensive investigation of the interface chemistry of Al rich Al–Fe alloys as a function of their chemical composition. Composition spread thin films with a linear composition gradient were produced by thermal codeposition. A scanning droplet cell was used to determine the open circuit potential and to perform successive anodic oxide formation with intermittent impedance spectroscopy. The film formation factor, the relative permittivity of the oxides and the onset potential of oxide formation were determined quantitatively as function of the composition with a resolution of 0.5 at.%. An unexpected synergistic effect is found in a very narrow composition range between 9 and 12 at.% Fe. This effect, which shifts the onset potential by nearly 1 V, is discussed in terms of a local accumulation of Fe resulting in a redox stabilisation of space charge layer formation during high-field oxide growth. The results are supported by composition and depth dependent XPS measurements.

Keywords: combinatorial libraries, scanning droplet cell, anodic oxide film, microelectrochemistry

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The development of alloys must have been purely empirical in ancient times. However, from an initial understanding of physical, chemical and metallurgical processes it has become a scientific discipline that uses gained knowledge for creating alloys with desired properties [1]. Nowadays, this further optimisation has many problems. A number of side effects such as synergistic amplification or annihilation can adversely affect the property, particularly if complex alloys with three or more elements are used. A systematic investigation of all possible combinations is no longer feasible. This has led to a renaissance of empirical alloy development, called combinatorial alloy development. The literature in this field is vast and only some aspects can be addressed here. Chang et al [2] investigated a library of 256 different doped (BaₓSr₁₋ₓ)TiO₃ thin films using a quaternary masking strategy performed during sputter deposition. Dielectric constant and tangent loss of these films were quantified, and tungsten was found to be the dopant that could most effectively minimize tangent loss. Measurements on the same system were performed by Pullar et al [3].

Van Dover et al [4] studied thin film dielectrics in the pseudoquaternary Zr–Sn–Ti–O system not only from a compositional point of view but also taking into account the effect of processing parameters. Combinatorial strategies were also applied to catalysis. Claus et al [5] applied scanning mass spectrometry to the analysis of reaction products on catalyst libraries, where each detection took only 60 s per catalyst. Liu et al [6] investigated the catalytic performance in terms of the oxygen reduction performance of Pt based and non-Pt based catalysts for applications in
European Society of Artificial Organs. PEMFC and DMFC. Fleischauer and co-workers developed useful techniques for combinatorial electrochemistry, namely, a multichannel pseudopotentiostat [7] and a 64 channel combinatorial electrochemical cell [8], their interest being mainly directed towards battery applications [9, 10]. Schuhmann and co-workers have developed a robotic system that allows not for only the fabrication but also the characterization of a library of 148 cathodic electrodeposition paints in terms of their biosensing properties [11]. Such a robotic system has also been used for the automated evaluation of corrosion properties, namely, the features of Ni release in electropolished NiTi samples [12]. Electroanalytical and electroanalytical techniques were realized using such a robotic system for combinatorial microelectrochemistry [13].

Potential fuel cell anode catalysts, namely, combinatorial libraries of Pt–Ru alloys were produced by sequential sputter deposition and evaluated by scanning electrochemical microscopy (SECM) [14].

Most of the aforementioned studies have focused on a single investigation technique rather than a comprehensive evaluation of the reactivity or passivity of the alloy and the forming surface films. Such an investigation is possible using a scanning droplet cell (SDC), which allows applying all common electrochemical techniques in a small area defined by the droplet wetting a surface [15]. Oxide formation and electrochemical impedance spectroscopy can be performed in the same area; this allows for the generation of a complete description of the electrochemical response of a given surface. This approach is being applied to binary Al–Fe samples ranging from 5 at.% Fe to 23 at.% Fe in this work. These studies are not only interesting in evaluating the properties of the alloys, which are gaining further interest as high temperature materials. A second important field in which this knowledge is relevant is that of structural joints such as welds between steel and aluminium in multmetal constructions such as modern car fabrication.

Mukai et al [16] studied the mechanical properties of electron beam deposited Al–Fe alloys with Fe contents between 1.15 and 1.71 at.% Fe. For the alloy with the highest Fe content, an abnormal high yield strength was observed. The unique mechanical properties were assigned to nanometre-sized subgrains along with a high angle grain structure.

Habazaki et al studied the anodisation of binary Al–Fe alloy containing 4 at.% Fe or 7.5 at.% Fe in an ammonium pentaborate solution [17, 18]. The samples were produced by sputtering deposition. Anodisation yielded an alumina film that was essentially free of Fe species. Instead, Fe accumulated in a sublayer 2–3 nm thick with a composition approximately that of the intermetallic phase Al13Fe2. Further oxidation led to a subsequent incorporation of Fe into the oxide formed. A very similar behaviour was observed by Hassel et al [19] during the oxidation of the equiatomic binary alloy NiTi, from which virtually Ni free Ti oxide layers were formed along with an intermetallic sublayer of the stoichiometry Ni3Ti.

Prudêncio et al [20] used high dose high energy implantation to demonstrate that the intermetallic disordered phase Al13Fe2 is initially formed. After annealing at 630 °C for 1 h, Fe diffuses to give an intermetallic compound with a lower Fe content of the nominal composition Al11Fe4 with a rod shaped micrometer-sized structure.

Thomas and Birss [21] compared the anodisation behaviour of bulk Al with a pure matrix version of an Al alloy containing Fe, V and Si with that of a two phase version in which the matrix and dispersoids are present. Although the electrochemical properties of bulk Al and the matrix version are comparable, the dispersoid showed the highest activity, an effect well known from corrosion investigations of Al alloys with intermetallic particles [22].

The aim of this work is to describe the electrochemical properties of oxide films formed on Al–Fe alloys. Laterally graded thin film samples with a spread in composition have been prepared by thermal co-evaporation and investigated by field emission scanning electron microscopy (FE-SEM), energy dispersive x-ray spectroscopy (EDX), scanning droplet cell (SDC) and x-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Al–Fe graded sample preparation

Silica microscope slides (76 × 26 × 1 mm2) were used as substrates for the thermal co-evaporation of Al and Fe thin films. The silica substrates were etched in a 3 : 1 mixture of H2SO4 and H2O2 for 50 min followed by deionized water rinsing and ultrasonic cleaning in an ethanol bath for 30 min prior to alloy deposition. The co-evaporation vacuum chamber had a base pressure of 2 × 10−4 Pa, which increased to 3.3 × 10−4 Pa during the deposition. Two thermal evaporation sources were used simultaneously for the evaporation of high purity (5 times zone-refined, in house production) Fe and Al (99.999%, Goodfellow) at room temperature to obtain a vapour phase mixed Al–Fe solid solution. Figure 1(a) shows the schematic of the co-evaporation setup. The distance between the sources and the substrate was 16 cm. Two crystal quartz monitors were used for the determination of the deposition rates of both metals and the power of the evaporation sources was adjusted accordingly to obtain the desired evaporation rates. This was achieved using a hardware PID-controller (proportional, integral, differential). Al was deposited at a rate of 1 nm s−1 while Fe at 0.5 nm s−1, the final thickness of the graded Fe–Al thin film being 300 nm. The thickness could be directly determined from the adjacent quartz crystal micro balances in the vacuum system, which allowed for the monitoring of not only the evaporation sources but also the thickness in the central part of the sample where mixed deposition took place. The thickness and deposition rate were independently confirmed by weight and chemical analysis. This was performed by cutting thin slices of the wafer and relating the weight to the area as determined by optical area recognition. Pieces of the wafer were individually boiled in hydrochloric acid to dissolve the entire metal film. The absolute amount of both metals was determined by inductively coupled optical emission spectroscopy (ICP-OES). After the deposition of the graded
alloy sample, energy dispersive x-ray spectroscopy (EDX) was used for the mapping of the component concentrations along the sample and in this way an Al concentration variation from 95 to 75 at.% was measured. This corresponds to a linear composition gradient of 2 at.% cm\(^{-1}\). In figure 1(b), the Al and Fe concentrations are shown as functions of the geometrical position on the surface of the sample. X-ray diffraction (XRD) analysis confirmed that a solid solution was obtained by this method and no hints of the formation of Al–Fe intermetallics were found.

2.2. Microelectrochemical cell description

For the growth and characterization of anodic oxides on the Al–Fe graded sample, a scanning droplet cell (SDC) was used [15]. The outer body of the cell was built from a capillary, 2.5 mm in diameter, which was pulled using a puller (PC-10, Narishige) and a tip with a diameter of 200 \(\mu\)m was obtained using a micro grinder (EG-400, Narishige). The reference electrode used was a capillary \(\mu\)-AuHg/Hg\(_2\)(CH\(_3\)COO)\(_2\)/Na(CH\(_3\)COO) reference electrode having a 1 mm outer diameter and a 100 \(\mu\)m tip diameter. A 1 mm wide Au band that was wrapped around the reference electrode capillary was used as the counter electrode. All components of the microelectrochemical cell were mounted into a plastic block. Details regarding the reference electrode and cell fabrication were previously reported [23–25]. A silicone gasket was fabricated at the tip of the cell by immersing it in liquid silicone followed by drying in nitrogen flow. To ensure a reproducible wetted surface (working electrode) on the graded Al–Fe sample, the tip of the cell was pressed against the investigated surface. In this way, the electrolyte air contact was severed and the expansion of the electrolyte droplet due to electrocapillarity during the measurements could be avoided [26].

2.3. Hardware description and measurements details

To dose the electrolyte from the cell, a computer controlled micro-syringe pump (Micro 4, World Precision Instruments) combined with a 100 \(\mu\)l syringe was used. The electrical contacting of the metallic surface was achieved using a tungsten needle pressed against the sample. The tip of the microelectrochemical cell could be randomly moved across the sample surface by a computer controlled 3D scanner actuating XYZ translation stages. Using the LabView control and data acquisition software developed in house, high throughput experimentation was achieved in an automatic manner. Details of the software can be found elsewhere [25]. A force sensor (KD45 2N, ME-Messsysteme) combined with a lock-in amplifier (EG & G 7265) was involved in the automated control of the applied force for pressing the tip of the microelectrochemical cell in a highly reproducible way, at a defined value of 3 mN against the sample. The laterally graded alloy surface was locally anodized along the composition gradient in an acetate buffer electrolyte (pH 6.0) prepared from p.a. chemicals and de-ionized water using a potentiostat (Solartron Schlumberger 1287). This acetate buffer was used since it falls exactly into the solubility minimum of Al and therefore yields the lowest corrosion rate and chemical stability, which is helpful when investigating the dielectric properties of the formed oxide films. Anodisation was carried out potentiodynamically at a potential scan rate of 100 mV s\(^{-1}\). All potentials are given versus that of the standard hydrogen electrode (SHE). Cyclic voltammograms having the upper potential limit between 1 and 10 V were sequentially recorded in 1 V steps for each investigated region. Before each cyclic voltammogram, the impedance of the oxide layer already formed by anodisation was measured using a frequency response analyzer with a 10 mV perturbation (S5720C, NF Electronic Instruments). X-ray photoelectron spectroscopy (XPS) was used for the in-depth qualitative evaluation of the Al–Fe graded sample at different compositions.

3. Results and discussion

3.1. Open circuit measurements

Using the above described alternation of cyclic voltammograms and impedance measurements, the surface of the Al–Fe graded sample was linearly scanned along the composition gradient with a resolution of 0.5 at.%. Figure 2 shows the open circuit potential (OCP) measured along the sample as a function of the Al concentration. After the initial contact of electrolyte with the surface of the sample, a stabilisation period of 150 s prior to the OCP measurement was used. The OCP measured on a pure Al thin film under the same
conditions is given as reference. The OCP initially increases gradually from approximately $-0.18 \, \text{V SHE}$ measured on pure Al and rather rapidly increase in the Al concentration interval between 92 and 85 at.% to a final anodic value of 0.35 V SHE. The OCP curve shows a distinct sigmoid shape connecting the two plateaus ranging from 0 to 6 at.% Fe and from 18–24 at.% Fe. The sigmoid shaped curve shown in figure 2 was calculated as a nonlinear least squares fit to a Boltzmann distribution function. The reference OCP measured on pure Al was not included in the fit and the trend of the OCP evolution towards lower Fe content alloys was suggested by the dotted line. A characteristic point of this curve is the point of inflection which is located at 11.8 at.% Fe and at an OCP of about 0.1 V. This sigmoid curve is quite common for the transition between two almost composition independent physical values. The percolation theory, which is based on the formation of a three dimensional network of the minor element in the matrix of the major element, predicts such behaviour. The point of inflection between two plateau values is commonly referred to as the percolation threshold. This idea was described earlier for stainless steels [27, 28].

3.2. Potentiodynamic oxide formation

In an attempt to make a complete electrochemical characterisation of Al–Fe alloys, a subsequent and alternating investigation of anodic oxide formation and impedance spectroscopy was performed. Each set of investigations was carried out on a different position on the sample equivalent to a stepwise increase in Fe concentration by 0.5 at.% This corresponds to nearly 400 potentiodynamic scans and the same number of impedance spectra. Thus, a complete graphical representation is impossible and a simplified one with only three representative compositions of 95, 90 and 85 at.% Al has been chosen in figure 3. A potential scan rate of 100 mV s$^{-1}$ was used and an impedance spectrum at 0 V was recorded after each potentiodynamic scan. The plateau current for each series of 1–10 V anodisation was considered as that measured in the cyclic voltammogram at 5 V since it was generally observed that this value represents a good average of all the individual plateaus.

The set of measurements for the 95 at.% Al composition is still very similar to that of pure Al. A sudden increase in current density is observed if the former oxide formation potential is exceeded and the current first increases to an absolute maximum before it falls to the plateau current. This maximum current corresponds to the so-called overshoot, an effect that is a direct result of the kinetic hindrance of the oxide formation due to the formation of a space charge layer, as described in the extended high field model [29]. This effect is less pronounced at higher potentials since the thicker oxide already on the surface causes a weaker field strength increase for a constant potential scan rate. At potentials higher than 6 V, this overshoot cannot be observed anymore since the retardation of the migrating ion clouds predominates the kinetics of oxide formation. This results in not only a smeared increase in oxide formation current but also a delayed increase, as can be directly seen from the increasing gap with increasing oxide formation potential between two subsequent oxide formation curves.

The second set of oxide formation curves shown in figure 3 corresponds to those for a composition of 90 at.% Al. The first difference observed is the delayed oxide formation compared with that for the 95 at.% Al composition. Furthermore, the initial overshoot is much more pronounced because it exceeds $500 \, \mu\text{A cm}^{-2}$. Then it shows a sudden drop that goes even below the plateau current. Generally, these curves show no overshoot, but have a tendency to be slightly higher in current. This change in shape is even stronger for the 85 at.% Al composition. Stronger current fluctuations indicate that alternative pathways of charge transport are starting to play a role. This is particularly observed in the last three curves that show a distinct current increase that may be attributed to a gas evolution occurring in parallel. Disregarding this assumption, a strict kinetic film formation analysis for all investigated compositions was performed.
A coulometric analysis of the potentiodynamic oxide formation or a determination of the plateau current in the potentiodynamic sweep allows calculating a film formation factor for each of the compositions investigated. To do so, the accumulated charge is plotted against oxide formation potential and the slope is used to determine the film formation factor according to

\[ q = K_{ox}^{-1} k E, \]

where \( K_{ox} \) is a material constant defined based on the density and molar mass of the oxide, its determination being described below, \( k \) is the formation factor expressed in nm V\(^{-1}\) and \( E \) is the potential. From the potentiodynamic scans, oxide plateau current may be determined, which can be directly used in the determination of \( k \) using a formula derived from the previous formula:

\[ k = i_{ox} K_{ox} v^{-1}, \]

where \( i_{ox} \) is the plateau current density and \( v \) is the rate of voltage increase during potentiodynamic scans.

To determine the material constant \( K_{ox} \) both, the density and the molar mass have to be taken into account. The density of the oxide and molar mass were calculated as functions of components concentration by means of a linear distribution between the densities or molar masses of pure Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) (5.25 and 3.5 g cm\(^{-3}\), respectively) according to the mixed matter theory. With an increase in the Fe content of the sample, oxidation current also increases. Figure 4 shows this film formation factors as a function of concentration. Up to 15 at.% Fe, a weak increase is observed from an initial value of 1.6 nm V\(^{-1}\) [30] to about 2.0 nm V\(^{-1}\). For higher Fe contents the nominal film formation factor increases more rapidly from 2.0 to 2.8 nm V\(^{-1}\) for Fe contents from 16 to 21 at.% Fe.

3.3. Initial film thickness

From the cyclic voltammograms in figure 3, certain passivity regions can be observed at the beginning of the oxide growth at different concentrations. These passive regions can be correlated with the presence of natural oxide on the surface of the sample before its anodisation. For the evaluation of these passive regions, the potentials at which the oxide begins to grow (the maximum potentials for the zero current) were determined from the cyclic voltammograms previously recorded. The moment of the oxide formation was determined as the beginning of the exponential increase in the current according to the high-field regime. The potentials corresponding to the middle of the exponential current increase (half wave potentials) were also measured, and the results were plotted in figure 5 as functions of the metal concentrations along the sample. For Fe concentration of up to 8 at.% a slight increase by less than 100 mV is observed. A marked increase by more than 1 V is found between 9 and 11 at.% Fe. After reaching the maximum at 11 at.% Fe, this potential decreases more quickly in the beginning by about 200 mV and then continues at a rate of about 30 mV at.\%\(^{-1}\) for the half wave potential. The final value obtained depends on the borderline concentration of the combinatorial sample investigated here. The half wave potential or the potential of current onset refers directly to the native oxide film on the sample. Since the history is identical for each point of the sample, the observed film thickness differences can be directly attributed to the difference in composition at this point of the sample. Pure Al forms a thin and very protective oxide film on the borderline concentration of the combinatorial sample investigated here. The half wave potential or the potential of current onset refers directly to the native oxide film on the sample.

This result is a prominent example of the advantage of combinatorial investigations over common batch sample.

![Figure 4](image-url) Oxide dielectric constant and oxide formation factors for different concentrations of alloys measured on surface of Al–Fe graded sample.

![Figure 5](image-url) Maximum potential for zero current and half wave potential as functions of metal concentrations in Fe–Al graded sample.
production. As long as there are no hints of behaviour in which a material shows an extreme value (here a maximum) of a property, there would be no reason to search in this concentration regime, thus the property would remain undiscovered. An additional advantage is the inherently equal treatment of various compositions in the combinatorial sample. Since the history of preparation, age surface treatment, air contact and other steps is identical, the differences found can be solely attributed to the differences in composition. For a set of batch samples, this would be usually not the case, and one may entertain some doubts whether or not an observed effect is caused by the difference in composition.

3.4. Impedance spectroscopy

Full impedance spectra were recorded at 0 V for several concentrations along the sample after the potentiodynamic growth of anodic oxides at 3 V. Three examples of these impedance spectra are shown in figure 6. Frequency was varied between \(2 \times 10^4\) and \(1 \times 10^{-1}\) Hz at a resolution of 10 measurements per decade. At a frequency of approximately 1 kHz, the phase shift between current and voltage reached a maximum for all the measurements, indicating that this frequency is suitable for capacitive measurement independent of metal concentration. At low frequencies, different values for the phase were observed and impedance decreased with an increase in Fe content.

The capacitance of the oxide layer was calculated from the impedance measurement at 1 kHz. Figure 7 shows examples of the relation between inverse capacitance and anodisation potential for the same selected compositions of 95, 90 and 85 at.% Al, as in figure 3. From the slopes of these curves, the relative permittivity number of the oxide layer, more commonly called dielectric constant, can be directly calculated as discussed in more detail in section 3.5.

An extrapolation of the reciprocal capacitance to zero, corresponding to the vanishing thickness of the anodic oxide, has, as a result, an oxide formation potential of about \(-2\) V. Taking into account the Helmholtz capacity with a value of 20 \(\mu\)F cm\(^{-2}\) for the series of the electrical double layer capacitance, previous results are matched in which the oxide formation potential on pure Al was found to be \(-1.6\) V [31, 32]. This is also seen from the position of the intersection of the three lines in figure 7.

3.5. Film formation factor and dielectric properties

Curves similar to those shown in figures 3 and 6 were recorded for each point from the full scan along the sample with a resolution in concentration of 0.5 at.%. The resulting oxide formation factors and dielectric constants are presented in figure 4 as functions of the composition. The experimental points were best fitted using multipeak Lorenztian distributions. The values measured on a pure Al thin film were added as reference. Both dielectric constant and oxide formation factor increase with an increase in Fe content. After a relatively slow increase in dielectric constant for Fe concentrations up to 8 at.%, a region of fast increase follows down to approximately 13 at.% Fe, matching the region of the fast increase in open circuit potential in figure 2. Between 13 and 18 at.% Fe, a dielectric constant plateau of 21, as well as a 2.1 nm V\(^{-1}\) plateau for the oxide formation factor could be observed. By further increasing Fe content, the gas evolution formation during the anodisation started to make the accurate calculations of dielectric constants and oxide formation factors more difficult. The drop in current efficiency under 100% is the most likely reason for the observed increase in Fe concentration over 18 at.%.
was added in order to compare the depths values with the total thickness calculated from the oxide formation factors. The investigated compositions (Al-7 at.% Fe, Al-10 at.% Fe and Al-16 at.% Fe) were chosen as representative for the three distinct regions shown in the dielectric constant plot of figure 4. From the spectra showing the $\text{Al}^0 - \text{Al}^{3+}$ 2p peaks, it seems that metallic Al was first found at depths of approximately 20 nm for the low Fe content regions, confirming the measured oxide formation factor in figure 4.

In the Al-16 at.% Fe region, no metallic Al was present at the same depth, most likely because the oxide formation factor for alloys of this composition is larger. The observation of the Fe spectra reveals two aspects of Fe atom dynamics in the modified Al oxide. Firstly, the depth at which metallic Fe was detected decreased with an increase in the Fe concentration of the alloy, confirming the idea that an Fe rich region is forming at the interface between the metal alloy and the anodic oxide even for this low anodisation potential (10 V) \[33\]. The

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**Figure 8.** XPS depth profiling of Al–Fe graded sample at different compositions.
presence of metallic Fe at approximately 5 nm depth in the Al-16 at.% region also shows that the Fe remains trapped inside the alumina layer without having a chance to react with oxygen ions in order to form oxide. On the other hand, Fe₂O₃ is present on the surface of the anodic oxides for 10 and 16 at.% Fe, vanishing rapidly with increasing depth in the intermediate case of Al-10 at.% Fe. The increase in the concentration of Fe₂O₃ on the surface is due to the more rapid outward migration of Fe ions than of Al ions [34] and in the case of the high Fe content Fe oxide can still be detected at depths as high as 20 nm, suggesting that Al oxide and Fe oxide are mixed in the anodic film.

4. Conclusions

A laterally graded sample ranging from the composition 95 at.% Al–5 at.% Fe on one side to 77 at.% Al–23 at.% Fe on the other side with a linear composition gradient of 2.57 at.% cm⁻¹ was prepared by thermal co-deposition. The alloy formed under these conditions is a solid solution and no intermetallic compounds are formed. The observed effects can therefore be assigned solely to the chemical gradient. The open circuit potential shows 2 plateau values at ~0.18 V SHE and 0.35 V SHE if plotted against composition. The transition is found at a composition close to 12 at.% Fe. Successive anodic oxidation with a resolution of 0.5 at.% Fe enables for a very distinct investigation of the effect of composition. A gradual influence on anodisation is observed, which affects the kinetics of oxide formation in the beginning and, for higher Fe contents, also the gas evolution kinetics of the oxide formed.

The apparent film formation factor including possible losses by side reactions increases from 1.6 to 2.8 nm V⁻¹ for the 23 at.% Fe content compared with that for bulk Al where the largest increase is found for values above 16 at.% Fe. Impedance spectroscopy enabled the determination of the capacitance. The reciprocal capacitance plotted against the film formation potential enabled the determination of the relative permittivity of the film. This increases from 12 on bulk aluminium to 25 for a 77 at.% Al–23 at.% Fe alloy.

A notable result is found in determining the onset of oxide formation from either the half wave potential or the potential at zero current as a function of composition. A very rapid increase is found when changing the composition by only 2 at.% from 9–11 at.% Fe. Surprisingly, a distinct maximum is observed for this composition of 89 at.% Al–11 at.% Fe. This behaviour is observed right before reaching the percolation threshold responsible for the highly nonlinear OCPs. Higher Fe contents will lead to lower onset potentials. This behaviour is assigned to an unexpected synergistic effect in which the Fe catalyses the oxidation in air with the formation of a thin protective aluminium oxide layer that shows a local enrichment of Fe. This local Fe enrichment confirmed by XPS depth profiling can probably stabilise the space charge layer that forms during the high field oxide growth, giving rise to an amplified current overshoot during initial oxide formation.

The method introduced here, combining samples with a lateral spread in the composition with scanning microelectrochemistry has a high potential for an efficient combinatorial development of advanced materials.

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References

[1] Agricola G 1556 De Re Metallica, Basel
[2] Chang H, Gao C, Takeuchi I, Yoo Y, Wang J, Schultz P G and Xiang X-D 1998 Appl. Phys. Lett. 72 2185
[3] Pullar R C et al 2007 J. Eur. Ceram. Soc. 27 4437
[4] van Dover R B, Schneemeyer L F, Fleming R M and Huggins H A 1998/1999 Biotechnol. Bioeng. 61 217
[5] Claus P, Hönicke D and Zech T 2001 Catal. Today 67 319
[6] Liu J H, Jeon M K and Woo S I 2006 Appl. Surf. Sci. 252 2580
[7] Cumyn V K, Fleischauer M D, Hatchard T D and Dahn J R 2003 Electrochem. Solid-State Lett. 6 E15
[8] Fleischauer M D, Hatchard T D, Rockwell G P, Topple J M, Trussler S, Jericho S K, Jericho M H and Dahn J R 2003 J. Electrochem. Soc. 150 A1465
[9] Hatchard T D, Topple J M, Fleischauer M D and Dahn J R 2003 Electrochem. Solid-State Lett. 6 A129
[10] Santamaria M, Di Quarto F, Skeldon P and Thompson G E 2006 J. Electrochem. Soc. 153 B515
[11] Reiter S, Ruhlig D, Ngounou B, Neugebauer S, Janiak S, Vilkanauksyte A, Erichsen T and Schumann W 2004 Macromol. Rapid Commun. 25 348
[12] Ruhlig D, Schulte A and Schumann W 2006 Electroanal. 18 53
[13] Erichsen T, Reiter S, Ryabova V, Bonsen E M and Schumann W 2005 Rev. Sci. Instrum. 76 062204–1
[14] Black M, Cooper J and McGinn P 2005 Meas. Sci. Technol. 16 174
[15] Hassel A W and Lohrengel M M 1997 Electrochim. Acta 42 3327
[16] Mukai T, Suresh S, Kita K, Sasaki H, Higashi K and Inoue A 2003 Acta Mater. 51 4197
[17] Habazaki H, Shimizu K, Skeldon P, Thompson G E and Wood G C 2001 Corros. Sci. 43 1393
[18] Habazaki H, Takahiro K, Yamaguchi S, Shimizu K, Skeldon P, Thompson G E and Wood G C 1999 J. Electrochem. Soc. 146 2502
[19] Hassel A W, Neelakantan L, Zelenkyvych A, Ruh A and Spiegel M 2008 Corros. Sci. 50 1368
[20] Prudencio L M, Nogueira I D, Waerenborgh J C, Goncalves A P, Conde O and da Silva R C 2002 Surf. Coat. Technol. 158–159 339
[21] Thomas S C and Birss V I 1997 J. Electrochem. Soc. 144 558
[22] Vander Kloe J, Hassel A W and Stratmann M 2005 Z. Phys. Chem. 219 1505
[23] Hassel A W, Fushimi K and Seo M 1999 Electrochem. Commun. 1 180
[24] Lili K A and Hassel A W 2006 J. Sol. State Electrochem. 10 941
[25] Mardare A I, Wieck A D and Hassel A W 2007 Electrochim. Acta 52 7865
[26] Lohrengel M M, Moehring A and Pilaski M 2001 *Electrochim. Acta* **47** 137

[27] Sieradzki K and Newman R C 1986 *J. Electrochem. Soc.* **133** 1979

[28] Fujimoto S, Newman R C, Smith G S, Kaye S P, Kheyrandish H and Colligon J S 1993 *Corros. Sci.* **35** 51

[29] Lohrengel M M 1993 *Mater. Sci. Eng.* **R11** 243

[30] Diesing D, Hassel A W and Lohrengel M M 1999 *Thin Solid Films* **342** 282

[31] Hassel A W 1993 *Diploma Thesis* Heinrich-Heine-Universität Düsseldorf, Germany

[32] Hassel A W and Lohrengel M M 1995 *Mater. Sci. Forum* **185–188** 581

[33] Habazaki H, Takahiro K, Yamaguchi S, Shimizu K, Skeldon P, Thompson G E and Wood G C 1999 *J. Electrochem. Soc.* **146** 2502

[34] Habazaki H, Shimizu K, Skeldon P, Thompson G E and Wood G C 2001 *Corros. Sci.* **43** 1393