Anodization of aluminium
Atomic simulations of the initial process steps

Master of Science Thesis

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In order to get a better control over the anodization process of aluminium, it is necessary to obtain a better understanding of the process at an atomic scale. In order to achieve this, molecular dynamics simulations are performed to study the reactions taking place during the initial formation of an anodic oxide layer, and to determine the influence of the electric field strength, temperature and environment on these reactions and the ion movement in the oxide layer. Simulations are performed regarding the oxidation of aluminium in an atomic oxygen environment under the influence of an external electric field, regarding the anodization of aluminium in water, in an oxalic acid solution and in an ammonium tartrate solution. It was found that applying a higher electric field strength only significantly influences the oxide thickness if this electric field strength is higher than a certain critical value. A higher temperature lowers this critical value. In an ammonium tartrate solution the tartrate ions assist in the formation of an oxide layer, leading to a thicker layer at a lower field strength as compared with anodization in pure water. To improve the modelling of the anodization process the charge equilibration procedure should be adjusted for a more realistic description of the charges and, with that, a more realistic description of the reactions that take place during the anodization process.
Preface

A year and a half ago I decided that it was finally time to finish what I started a long, long time ago. After I obtained my bachelor’s degree in mechanical engineering in Eindhoven and performed a part of the master program, I had taken a long break to take care of my children. Now it felt like a good time to study again and obtain my master’s degree in mechanical engineering in Delft.

I would like to thank my supervisor Barend Thijsse for giving me the opportunity to perform the research for this Master Thesis in his group. It was really motivating to work with someone who is always enthusiastic about the obtained results even though they are not always as promising as I would have liked. Without the help of Fidel Valega Mackenzie I would not have come as far as I am now. He taught me all the ins and outs of LAMMPS and was always there to answer my questions. During my time in Delft I shared an office with several people: Robbert-Jan Dikken, Dennis Braekmans, Fidel Valega Mackenzie and Neha Verma. I am really grateful for their company, their help with printing and of course the many cups of coffee. And when none of my roommates was present, there was always Anke Kerklaan-Koene, for a chat or a cup of coffee.

Being a student and a parent is not always the most practical combination, but luckily I could always rely on my parents, Ben and Adje Elzas, and my parents-in-law, Ger and José Gubbels, for practical assistance during the school holidays. My mother deserves a much larger thanks than I can express in words. She came every Wednesday afternoon and on so many of those days the children had an extra day off from school, to take care of them, bring them to their music lessons, practice their schoolwork with them and so much more.

My children, Lieke, Thomas and Martin, were of course not always happy that I had less time available for them than before, but they also kept motivating me by telling me I should really graduate. Without the constant love and support of my husband Guido I probably would not even have started in Delft and it would have definitely taken me much longer to finish this thesis.
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Chapter 1

Introduction

Under environmental conditions aluminium readily reacts with the oxygen in air to form an oxide layer. This layer is typically a few nanometers thick and has an amorphous structure. The oxide layer protects the aluminium against further reactions with the environment and will therefore serve as an electrical insulator. Since this layer is very thin and can easily spell off, it often will be necessary to increase the corrosion resistance, surface hardness and appearance of an aluminium product.

To enhance the properties of the oxide layer, such as the structure and the thickness, use can be made of a process called anodization. This is an electrochemical process in which the aluminium is placed in an aqueous electrolyte bath, as is shown in Figure 1.1.

![Figure 1.1: Schematic representation of anodization process.](image)

\[ 2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2 \]

The aluminium is made the anode in the anodizing cell by connecting it to the positive terminal of a power supply. The cathode is formed by a plate or rod that is placed in the anodizing bath and connected to the negative terminal of the power supply. The plate or rod is made of a material that is inert in the anodizing bath. If the power is switched on the circuit is closed. Electrons are withdrawn from the aluminium leaving aluminium ions that can either react at the aluminium/oxide interface with oxygen ions to form aluminium oxide or travel through the oxide layer and react at
the oxide/electrolyte interface with water to form aluminium oxide. At the side of the cathode the electrons return to the bath, where they react with hydrogen ions to form hydrogen gas.

The type of oxide layer that forms, whether it is a dense barrier layer or a porous oxide layer, is primarily determined by the composition of the electrolyte. A near neutral electrolyte leads to the formation of a dense barrier layer. The use of an acidic electrolyte leads to a porous oxide layer. The formation of this porous oxide layer is characterized by the formation of aluminium oxide, or alumina, together with the dissolution of aluminium oxide into the electrolyte.

The nature of the acid, its concentration, the applied field strength and the anodizing time all influence the structure and thickness of the resulting oxide layer. Since aluminium reacts so easily with the oxygen in air to form an oxide layer, in practice aluminium will always be covered with a native oxide layer prior to the anodization process. The structure of this native oxide layer will also influence the structure of the oxide layer formed by anodization.

A barrier layer formed by anodization can be up to one µm thick. Compared with the 2 - 3 nm formed under ambient conditions this is 300 to 500 times as thick. A barrier oxide formed by anodizing can support an electric field strength in the order of 1 V/nm [1].

A porous anodic aluminium oxide formed by anodization typically has a hexagonal ordered pattern of nanopores, Figure 1.2. The oxide layer consists of hexagonal cells with pores at the center of each cell. These deep pores have a hemispherical bottom consisting of a barrier oxide layer. The size and ordering of these pores as well as the structure and thickness of the oxide layer are determined by the process conditions. A porous alumina layer can be up to 100 µm thick. The cell diameter can vary between 50 and 300 nm, while the pore diameter will be one third till one half of the cell diameter. The cell population density can vary between 10 till more than 100 per µm². The aspect ratio of the pores can be as large as 1000:1 [1].

![Figure 1.2: Idealized structure of porous aluminium oxide, from [2].](image)

The formation of these pores results from the roughness of the aluminium surface, leading to a non-uniform oxide layer. Combined with the dissolution of alumina in the electrolyte this can results in a porous structure. To describe the formation as well as the self-adjustment of these pores, several models have been derived. A majority of this models is based on the mechanical stress associated with the formation of aluminium oxide. When oxygen enters the close-packed aluminium crystal the combination of aluminium and oxygen will occupy a larger volume in space than the bare aluminium. This change in volume when going from metal to oxide is described by the Pilling-Bedworth ratio

$$R_{PB} = \frac{V_{oxide}}{V_{metal}}.$$ (1.1)

For α-Al₂O₃ the Pilling-Bedworth ratio has a value of 1.28. This value is based on measurements of the mass and density of an oxide [3]. Since the volume occupied by aluminium oxide is larger than the volume occupied by the aluminium needed to form this oxide, this leads to mechanical
stresses in the material. The repulsive force between neighbouring pores leads to the self-ordering of these pores.

O’Sullivan and Wood [4] described a steady-state in the pore formation to be an equilibrium between growth of the oxide layer at the metal-oxide interface and dissolution of the oxide at the oxide-electrolyte interface of the barrier layer at the bottom of the pore. In this steady-state the thickening of the porous oxide layer proceeds at a constant rate while the thickness of the barrier layer remains constant.

Jessensky et al. [5] show the size of ordered domains on anodic alumina to depend on the anodizing voltage. This correlates with the voltage dependence of the volume expansion in the formation of aluminium oxide. Only moderate expansion of aluminium in the formation of alumina leads to an ordered pore structure. The mechanical stress resulting from the expansion of aluminium during oxide formation causes repulsive forces between neighbouring pores leading to a hexagonal ordering of pores.

The relation between the applied voltage $U$, the thickness $d$ of the oxide layer and the electric field strength $E$ in the oxide layer is given by

$$E = U/d.$$  (1.2)

The field strength in the oxide layer has to be above a certain critical value in order to drive the ions through the oxide layer. If the field strength drops below this critical value the oxidation stops. For a constant voltage being applied, there will be a maximum thickness associated with that voltage that can be reached, according to equation 1.2. In parts of the oxide layer with a lower thickness there will be a higher field strength leading to growth of the oxide layer, which in turn leads to a lower field strength. Eventually everywhere in the film the same thickness $d_c$ and field strength $E_c$ will be reached. This is the basis of the equifield strength model proposed by Su et al. [6], to describe the experimental observations regarding pore growth, pore morphology and porosity. This model is based on oxidation of metal by $O^{2-}$ and $OH^-$ and dissolution of oxides. If in the initial flat oxide layer on an aluminium surface, Figure 1.3a, a pit forms, Figure 1.3b, the electric field strength is no longer uniform in the oxide layer, if a constant voltage is applied. At the thinner part of the oxide layer, B'-B, the field strength is higher than at the thicker parts, A'-A and C'-C. This leads to increased growth in this thinner part of the oxide layer, until a uniform field strength is obtained. The hemispherical pit is reproduced at the aluminium-oxide interface, Figure 1.3c. Dissolution of oxide at the oxide-electrolyte interface and growth of the oxide at the aluminium-oxide interface then leads to the formation of a pore, Figure 1.3d. The initial pit can result from defects in the oxide layer as well as the aluminium, such as impurities, dislocations, grain boundaries and nonmetallic inclusions. The rough surface of the native oxide layer can also contribute to the formation of a pit.

Oh and Thompson [7] show that the dissolution rate of aluminium oxide is enhanced by the electric field leading to disordered pores with relatively small spacings above the critical field strength. Mechanical instability associated with plastic deformation, and not a field-induced instability, leads to larger-scale ordered structures.

For the growth of barrier layers Hebert and Houser [8] developed a model that describes the transport in planar anodic films. In their model ion migration is driven by gradients of mechanical stress and electrical potential.

Although intensive research has been done to the formation and self-ordering of pores in an anodic alumina layer, there is still a lot unknown with respect to the actual ion movement in the formation and growth of an anodic oxide layer and the influence of the process conditions such as environment and temperature on the resulting structure. Anodization is an energy-intensive process. If the process would be better understood, the efficiency could be enhanced [9]. Anodization is employed to enhance the corrosion resistance of products, to increase abrasion wear resistance and to create decorative layers by incorporation of organic or metallic pigments in the pores, before sealing the layer. Anodic alumina is used for the production of dielectric films that are used in
Figure 1.3: Formation of a pore in an oxide layer on an aluminium surface. If in the initial flat oxide layer, Figure 1.3a, a pit forms, Figure 1.3b, the electric field strength is no longer uniform in the oxide layer, if a constant voltage is applied. At the thinner part of the oxide layer, B'-B, the field strength is higher than at the thicker parts, A'-A and C'-C. This leads to increased growth in this thinner part of the oxide layer, until a uniform field strength is obtained. The hemispherical pit is reproduced at the aluminium-oxide interface, Figure 1.3c. Dissolution of oxide at the oxide-electrolyte interface and growth of the oxide at the aluminium-oxide interface then leads to the formation of a pore, Figure 1.3d, from [6].

electrolytic capacitors. Anodization of aluminium is one of the most frequently used methods for the synthesis of ordered nanostructures [10]. Given the wide-spread use of anodic alumina, a better process control would lead to massive energy reductions. Furthermore, since pore structures grown by anodizing aluminium are used as template for producing nanowires and nanotubes, an increased understanding of the process would accommodate further progress in this area.

Different studies regarding the oxidation of aluminium on an atomic scale have been reported in literature [11, 12, 13, 14]. The effect of an applied electric field on the growth and/or ion transport in an oxide layer is studied for different metals. The effect of an electric field on the oxidation behaviour of aluminium is studied [15]. The ion transport in the pore surface of a porous anodic alumina is investigated with molecular dynamics simulations [16]. The influence of an applied electric field on the oxidation behaviour of zirconia is studied [17], as well as on the oxidation of nickel in pure water [18]. The oxidation behaviour of iron is studied under the influence of different temperatures and electric field strengths [19].

In this study, to enhance the understanding of the anodization process of aluminium, the initial steps of this process are modelled on an atomic scale with molecular dynamics simulations. The influence of process conditions on the resulting oxide layers and the mechanisms contributing to the formation of these layers are studied. The methods used to perform this study are explained in chapter 2, as well as the general setup of the simulations. The influence of both electric field and temperature on ion transport through the oxide layer are studied in chapter 3. The start of the oxidation process in the presence of water, a strong acid solution or a near neutral acid solution and the influence of the electric field on the initiation and growth of the oxide layer in these environments is studied in chapters 4, 5 and 6. The dissociation of water at a bare aluminium surface as well as at a native oxide layer and the influence of an electric field on this process are studied, as well as the resulting structure of the oxide layer. In chapter 7 a modification of the implementation of an electric field in the software is proposed in order to model the influence of the electric field more accurately, some problems regarding the determination of charges in the model are discussed and a comparison with an alternative force field is made. Finally, in chapter 8, some conclusions are drawn based on this study and recommendations for further research are given.
Chapter 2

Methods

To study the first steps of the anodization process, the process is modelled on an atomic scale. This is done with molecular dynamics simulations. The system configuration is modelled in Aten [20]. With this configuration simulations are performed in LAMMPS [21, 22]. Visualization of the system is done again in Aten and the post processing is done with the aid of MATLAB.

In this chapter the theory behind the molecular dynamics simulations, the force field applied in the simulations and the determination of the atomic charges in the simulations is explained. The implementation of an electric field in the molecular dynamics simulations and the general setup of the simulations is described. In chapter 7 the implementation of an electric field and the determination of the atomic charges are discussed in more detail.

2.1 Molecular dynamics

In order to perform molecular dynamics simulations a system of atoms is modelled of which both the initial positions and the initial velocities of the atoms are known. The potential energy of such a configuration is described by the so-called potential $V$, which is a function of the positions of the atoms. The force on each atom is then given by the gradient of this potential with respect to the positions of the atoms,

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V(\mathbf{r}_1, ..., \mathbf{r}_N). \quad (2.1)$$

To obtain the positions at time $t + \Delta t$ from the positions at time $t$, a velocity Verlet scheme is used [23],

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2,$$

$$\mathbf{v}(t + \Delta t/2) = \mathbf{v}(t) + (1/2)\mathbf{a}(t)\Delta t,$$

$$\mathbf{a}(t + \Delta t) = -(1/m)\nabla V(\mathbf{r}(t + \Delta t)),$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t + \Delta t/2) + (1/2)\mathbf{a}(t + \Delta t)\Delta t. \quad (2.2)$$

2.2 ReaxFF

How accurately the interactions between the atoms of the system are described, depends on the chosen potential. In this study use is made of a reactive forcefield ReaxFF [24] [25]. This force field is developed to adequately describe the formation and dissociation of chemical bonds. To achieve this, the bond-order of each atom pair is determined from its instantaneous inter atomic distance. This bond-order is updated every time step. The energy of the total system is tallied down in different energy contributions,

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{con}} + E_{\text{vdW}} + E_{\text{Coulomb}}. \quad (2.3)$$
The bond energy \( E_{\text{bond}} \) is dependent on the bond order. The terms \( E_{\overline{\text{over}}} \) and \( E_{\overline{\text{under}}} \) are included to correct for over- and undercoordination. The energy associated with lone electron pairs, \( E_{\text{lp}} \), is included to take into account the influence these lone pairs on heteroatoms, such as nitrogen and oxygen, can have on the response to over- and undercoordination. The valence angles around atoms can be influenced by these lone pairs and they can contribute to the stability of a conjugated system by delocalizing. The energy associated with deviations in the valence angle from the equilibrium value, \( E_{\text{val}} \), and the additional energy penalty \( E_{\text{pen}} \), which is imposed on a system which includes two double bonds sharing an atom in a valence angle to reproduce stability, are both dependent on the bond order to ensure these contributions disappear on breaking of the bond. The contributions from the torsion energy \( E_{\text{tors}} \) and the conjugation energy \( E_{\text{conj}} \) are also ensured to disappear upon breaking of a bond by making them dependent on the bond order.

During a simulation there will be a constant breaking and formation of bonds. The van der Waals and Coulomb interactions, \( E_{\text{vdW}} \) and \( E_{\text{Coulomb}} \), can therefore not be excluded for bonded atom pairs. Both the van der Waals and Coulomb energy are therefore included for all atom pairs independent of their connectivity. The van der Waals energy is a distance-corrected Morse potential. The interaction is shielded to avoid excessively high repulsions between bonded atoms and atoms sharing a valence angle. The Coulomb energy is shielded to adjust for orbital overlap between atoms at close distances. It is dependent on the charges of the atoms. These charges are determined with a charge equilibration procedure QEq \[26\], as described in section 2.3.

Two parameterizations of ReaxFF are used in this study. A parametrization including aluminium, oxygen and hydrogen is used \[27\] if no other elements where used in a simulation. In simulations where there is an acid involved, the parametrization by Valega and Thijsse is used \[28\], which regarding aluminium, oxygen and hydrogen is similar to the first parameterization, but includes nitrogen and carbon, next to aluminium, oxygen and hydrogen. In both these parameterizations the cut-off radius for non-bonded interactions, being the Coulomb and van der Waals energy from equation 2.3, is set to 10 Å. The other terms from equation 2.3 are bond-order dependent. The bond-order cut-off to determine if atoms are connected is set to 0.1000.

2.3 Charge equilibration procedure

To determine the charge of each atom a charge equilibration procedure QEq is used \[26\]. With this procedure, the charges are determined based on geometry and experimental atomic properties.

The change in energy \( E \) of an isolated atom \( A \) as a function of the charge \( Q \) with respect to a neutral reference point \( E_{A_0} \) is given by

\[
E_A(Q) = E_{A_0} + Q_A \left( \frac{\partial E}{\partial Q} \right)_{A_0} + \frac{1}{2} Q^2 \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A_0} + \ldots . \tag{2.4}
\]

If only terms through second order are included, this leads to

\[
E_A(+1) = E_{A_0} + \left( \frac{\partial E}{\partial Q} \right)_{A_0} + \frac{1}{2} \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A_0} = E_{A_0} + IP, \\
E_A(0) = E_{A_0}, \\
E_A(-1) = E_{A_0} - \left( \frac{\partial E}{\partial Q} \right)_{A_0} + \frac{1}{2} \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A_0} = E_{A_0} - EA, \tag{2.5}
\]

where \( IP \) is the ionization potential and \( EA \) stands for the electron affinity. From equation 2.5 it follows that
\[ \left( \frac{\partial E}{\partial Q} \right)_{A_0} = \frac{1}{2} (IP + EA) = \chi_A^0, \]

\[ \left( \frac{\partial^2 E}{\partial Q^2} \right)_{A_0} = IP - EA = J_{AA}^0, \] (2.6)

where \( \chi_A^0 \) is the electronegativity and \( J_{AA}^0 \) is referred to in literature as idempotential, self-Coulomb potential or hardness. In this study it will be referred to as self-Coulomb potential. Equation 2.4 can than be written as

\[ E_A(Q) = E_{A_0} + \chi_A^0 Q_A + 1/2 J_{AA}^0 Q_A^2. \] (2.7)

To determine the energy of a system of charges, the interatomic electrostatic energy should be taken into account.

\[ E(Q_1, \ldots, Q_N) = \sum_A \left( E_{A_0} + \chi_A^0 Q_A + 1/2 Q_A^2 J_{AA}^0 \right) + \sum_{A \neq B} Q_A Q_B J_{AB}, \] (2.8)

where \( J_{AB} \) is the Coulomb interaction between unit charges on centers A and B, dependent on the distance between A and B.

\[ J_{AB} = \frac{14.4}{R}, \] (2.9)

where R is the distance between centers A and B. The factor 14.4 is a conversion factor to convert R in Å to \( J_{AB} \) in eV. Equation 2.9 leads to \( J_{AB} \) going to infinity when \( R \) goes to zero. Since \( J_{AB} \) should go to finite values, related to \( J_{AA} \) and \( J_{BB} \), a shielding correction is applied to the Coulomb interaction for distances where the charge distributions on centers A and B overlap. This shielding correction is expressed as the Coulomb integral between atomic densities, which are described in terms of a single Slater orbital, as described by Rappé and Goddard [26].

The derivative of the energy with respect to the charge of a specific atom is the atomic-scale potential \( \chi_A(Q_1, \ldots, Q_N) \),

\[ \chi_A(Q_1, \ldots, Q_N) = \frac{\partial E}{\partial Q_A} = \chi_A^0 + J_{AA}^0 Q_A + \sum_{B \neq A} J_{AB} Q_B. \] (2.10)

In order to have equilibrium this atomic-scale potential has to be equal for each atom,

\[ \chi_1 = \chi_2 = \ldots = \chi_N. \] (2.11)

For a system with N atoms this leads to N-1 conditions. The charge of the total system is not allowed to change,

\[ Q_{\text{tot}} = \sum_{i=1}^{N} Q_i = 0, \] (2.12)

leading to N conditions that have to be solved for a system. These conditions are implemented in LAMMPS as described in [29]. The actual values for the electronegativity and the idempotential are, among many others, the parameters that have to be fitted for each combination of elements. These are given in the ReaxFF force-field files, which are included in appendices A and B.

### 2.4 Implementation of electric field

Placing an external potential \( \phi \) on a system in LAMMPS is done by placing an electric field \( \mathbf{E} \) on that system. The relation between the electric field and the external potential is given by
\[ E = -\nabla \phi. \]  

This electric field is represented in the simulations by a force \( F \) proportional to the field strength and the charge \( Q \) of the particle it works on,

\[ F = QE. \]

### 2.5 Setup of simulations

To perform molecular dynamics simulations a system is modelled in Aten consisting of either only a slab of aluminium atoms or an aluminium slab and water or an acid dissolved in water. The aluminium slab has a FCC structure and a lattice constant of 4.041 Å at 300 K [30]. The initial velocity of the atoms in the simulation is set as a Gaussian distribution of velocities around the temperature at which the simulation is performed. All simulations are performed with a time step of 0.1 fs, to correctly capture the atom movements. The temperature is controlled by a Langevin thermostat [31]. During the simulations the volume of the system is kept constant. In all cases the aluminium and if present the water or acid solution are let to relax before starting the actual simulation.
Chapter 3

Oxidation of aluminium in an atomic oxygen environment

Under environmental conditions the oxidation of aluminium proceeds in a molecular oxygen environment. The start of the oxidation process is determined by the dissociation of oxygen molecules at the aluminium surface. This is a process with a low probability at room temperature, \( \leq 10^{-2} \) [32]. This low dissociation probability will influence the initial oxidation rate. In the presence of atomic oxygen no dissociation of a molecule is needed to provide the oxygen for the formation of an oxide layer and therefore the rate determining step in the oxidation process is expected to be the ion movement through the oxide layer. To study the influence of both an applied electric field and temperature on the ion movement in the oxide layer during the oxidation process, simulations are performed regarding the formation of an oxide layer on top of an aluminium slab in an atomic oxygen environment under the influence of an electric field and at different temperatures.

In this chapter the setup of the simulations with an aluminium slab and atomic oxygen will be described. The results of the simulations are given and the influence of both temperature and electric field strength on the resulting thickness of the oxide layer, on the ion movement in the oxide layer as well as on the resulting structure of the oxide layer is explained.

3.1 Setup of simulations with atomic oxygen

All simulations are performed with a slab of 1000 aluminium atoms which measures \( 20.2 \times 20.2 \times 38.4 \) Å\(^3\). This slab has periodic boundary conditions in x-, y- and z-direction and the top surface in the z-direction is the (100) surface. First this slab is let to relax at 300, respectively 600 K, under NPT conditions, keeping the number of atoms (N) the pressure (P) and the temperature (T) constant. After 10 ps of simulated time with a time step of 1 fs an equilibrium state was reached. The box is then enlarged in z-direction to account for oxygen being placed above the aluminium. The periodic boundary condition in z-direction is removed and replaced by reflecting walls to prevent the atoms from escaping the simulation box.

The atomic oxygen environment is modelled by introducing oxygen atoms in the simulation box with a constant frequency at a certain distance above the aluminium slab and a velocity directed towards the aluminium. An earlier study has shown this to be a convenient way of modelling an atomic gas [30]. The frequency to insert an oxygen atom in the simulation box is determined by the theoretic collision frequency of an atom from a gas with a wall. This collision frequency \( Z_{\text{wall}} \) is given by the Hertz-Knudsen equation,

\[
Z_{\text{wall}} = \frac{p}{(2\pi mk_B T)^{1/2}},
\]

where \( p \) is the pressure, \( m \) is the mass of the atom, \( k_B \) is the Boltzmann constant and \( T \) is the temperature.
After relaxation of the aluminium slab at 300 respectively 600 K, the surface measures 20.57 × 20.57 respectively 20.60 × 20.60 Å². To simulate an oxygen pressure of 1 atm at 300 K an oxygen atom is added to the simulation box every 190 fs. At 600 K an oxygen atom is inserted in the simulation box every 271 fs. The atoms are placed at a random (x,y)-position in the box at 4 Å above the surface, with a downwards velocity of 684 m/s at 300 K and 967 m/s at 600 K which represents the root mean square velocity of oxygen atoms at the given temperature.

Since the simulation box is bounded by reflecting walls in the z-direction, oxygen atoms that are not adsorbed and bounce back in the gas phase are confined in a small region above the aluminium surface. This could lead to accumulation of oxygen in a region determined through the size of the simulation box. To prevent accumulation of oxygen in the region above the surface, oxygen atoms that are not adsorbed at the surface, are removed from the simulation box every 100 fs.

To prevent displacement of the aluminium slab the bottom aluminium layer is kept fixed. Simulations are performed with a constant volume at 300 and 600 K with field strengths of 0.0, 0.5, 1.0, 1.5 and 2.0 V/Å and a time step of 0.1 fs. The simulations lasted 1000 ps. A schematic representation of the setup of the simulation is given in Figure 3.1.

Figure 3.1: Schematic representation of setup for simulations with an aluminium slab of 1000 atoms, where the top surface is the (100) surface, and a deposition of oxygen atoms. The y-direction is perpendicular to the plane of the paper.

The electric field is placed only over the oxide layer, which is formed during the simulation. To ensure this, it is necessary to define which atoms are part of the oxide layer. In order to do this, first the equilibrium aluminium-oxygen bond length is determined from the simulation regarding the oxidation of aluminium, without the presence of an electric field. This bond length measures 1.95 Å. To account for variations in the bond length due to vibrations of the atoms, a cutoff value for the bond-length is set at 2.0 Å.

In order to define the boundary between the aluminium slab and the oxide layer, the position of the lowest oxygen atom is determined. If an oxide layer exists, this lowest oxygen atom will be part of the oxide layer. An aluminium atom bonded to this oxygen atom but at a lower z-position can still be considered part of the oxide layer, since there will have been charge transferred between the oxygen atom and this aluminium atom. The lower boundary of the oxide layer is therefore defined to be the z-position of the lowest oxygen atom minus the cutoff value based on the equilibrium aluminium-oxygen bond length in the aluminium oxide, as can be seen in Figure 3.2.
Figure 3.2: Determination of region in which electric field acts. The region is confined between the z-position of the highest aluminium atom plus a cutoff based on the equilibrium Al-O bond length in alumina and the z-position of the lowest oxygen atom minus the same cutoff. The cutoff value equals 2.0 Å. Blue spheres represent aluminium, red spheres represent oxygen.

To define the boundary between the oxide layer and the oxygen gas, the position of the highest aluminium atom is determined. An oxygen atom at a higher z-position bonded to this aluminium atom will be part of the oxide layer. The upper boundary of the oxide layer is therefore defined to be the z-position of the highest aluminium atom plus the same cutoff value. The oxide layer is thus defined to be the region within the z-position of the lowest oxygen atom minus 2.0 Å and the z-position of the highest aluminium atom plus 2.0 Å, as can be seen in Figure 3.2.

3.2 Results of simulations with atomic oxygen

In the absence of an electric field it can be seen that oxygen atoms do not land at completely random positions at the surface, as earlier described [30]. The first oxygen atoms that enter the simulation box will land at a random position at the aluminium surface resulting in charge transfer between the oxygen atom and the aluminium atoms next to it. New oxygen atoms approaching the surface will, if close enough, feel an attraction from the positively charged aluminium and will preferentially land next to such a positively charged aluminium atom, at a different side then where the former oxygen atom landed. This will cause charge transfer between the new arriving oxygen and the already positively charged aluminium, leading to a more positively charged aluminium ion. The presence of oxygen ions surrounding the aluminium ion in the surface layer leads to the aluminium ion being pushed up, out of the surface layer, since this gives a more stable position for the ions. This aluminium ion will then attract another oxygen atom, get even more positively charged, and attract yet another oxygen atom. This results in small islands of aluminium atoms surrounded by three oxygen atoms in the surface layer and one oxygen atom at the top position, as shown for the aluminium (111) surface in Figures 3.3 and 3.4.

The formation of an oxide layer on FCC aluminium by atomic oxygen proceeds not at a constant rate. In Figure 3.5, for the aluminium (100) surface, the number of adsorbed oxygen atoms, which are all oxygen atoms at the aluminium surface or migrated inwards in the aluminium slab, is shown with respect to time. In Figure 3.6 different stages in the formation, as marked in Figure 3.5, are shown. Starting with a bare aluminium surface at 0 ps, Figure 3.6a, the rate of oxygen adsorption is initially high, reflecting the fact that all oxygen is adsorbed by the bare aluminium surface, Figure 3.6b at 13 ps. The adsorbed oxygen atoms force some of the aluminium atoms to move up, which results in new adsorption sites for the oxygen atoms, Figure 3.6c at 60 ps. At
Figure 3.3: Top view of aluminium (111) surface at different steps in a simulation at 300 K with deposition frequency of oxygen atoms reflecting an atomic oxygen gas with a density of 0.01 g/cm$^3$. Blue spheres represent aluminium and red spheres represent oxygen. [30]

Figure 3.4: Side view of aluminium (111) surface at different steps in a simulation at 300 K with deposition frequency of oxygen atoms reflecting an atomic oxygen gas with a density of 0.01 g/cm$^3$. Blue spheres represent aluminium and red spheres represent oxygen. [30]

the same time the adsorbed oxygen atoms repel other oxygen atoms approaching the aluminium. From the decrease in the adsorption rate at 200 ps, Figure 3.6d, it can be seen that the latter effect outweighs the former. When more oxygen atoms get adsorbed in the aluminium, the number of available adsorption sites decreases, as can be seen by the continuous decrease in adsorption rate until the end of the simulation at 1000 ps, Figure 3.6e.

### 3.2.1 Influence of electric field

The influence of an electric field on the formation of an aluminium oxide layer in an atomic oxygen environment can be clearly seen from Figures 3.7, 3.8 and 3.9. At 300 K for field strengths up to
Figure 3.5: Number of adsorbed oxygen atoms with respect to time, for a simulation with an aluminium slab with the (100) surface facing up and atomic oxygen at 300 K without an electric field applied. The configurations at the marked points in time are shown in Figure 3.6.

(a) 0 ps  (b) 13 ps  (c) 60 ps  (d) 200 ps  (e) 1000 ps

Figure 3.6: Side view of aluminium slab with the (100) surface facing up at different stages in the oxidation process, as marked in Figure 3.5, for the simulation with an aluminium slab and atomic oxygen at 300 K without an electric field applied. Blue spheres represent aluminium and red spheres represent oxygen.

At a field strength of 1.5 V/Å the curves showing the number of adsorbed oxygen atoms versus time all have the same shape, Figure 3.7a. Only the initial decrease in adsorption rate sets in at a later moment in time, as can be seen in Figure 3.8 where the first 100 ps of the simulations are shown. This indicates that only the initial adsorption is influenced by the electric field at these field strengths. At a field strength of 2.0 V/Å however, a strong influence of the field can be seen. After the initial decrease
in adsorption rate, the number of adsorbed atoms grows approximately linear with time until the end of the simulation at 1000 ps.

Figure 3.7: Number of adsorbed oxygen atoms versus time for simulations with an aluminium slab and a deposition of oxygen atoms at different electric field strengths and temperatures.

Figure 3.8: Number of adsorbed oxygen atoms versus time for first 100 ps of simulations with an aluminium slab and a deposition of oxygen atoms at different electric field strengths and temperatures.

The thickness of the oxide layer is defined as the difference between the average height of the five highest aluminium atoms and the average height of the five lowest oxygen atoms. The thickness of the oxide layer grows quite similar to the number of adsorbed oxygen atoms, Figure 3.9. Averages are used to determine the overall thickness of the oxide layer. The real thickness is not always equally distributed along the surface during the oxidation process. The adsorption of an oxygen atom at a lower part of the surface therefore will not always result in an increase in thickness of the oxide layer. This can be seen by comparing Figures 3.7 and 3.9.

At 600 K the adsorption rate is increased both by temperature and by the electric field. Figures 3.7b and 3.8b clearly show three different regimes regarding the influence of the electric field on the oxidation process. A field strength of 0.5 V/Å only influences the moment where the initial decrease in adsorption rate sets in, with respect to oxidation without an electric field applied, resulting in a curve with the same shape as without a field. A field strength of 1.0 V/Å leads to a
Figure 3.9: Thickness of oxide layer versus time for simulations with an aluminium slab and a deposition of oxygen atoms at different electric field strengths and temperatures.

constant adsorption rate, after the first decrease in adsorption rate, which is much higher than at lower field strengths. An increase in field strength to 1.5 V/Å only influences the initial adsorption relative to a field strength of 1.0 V/Å. A field strength of 2.0 V/Å has a major influence on the adsorption rate. The total number of adsorbed atoms at 1000 ps is approximately four times as high as without a field and the rate at this point is approximately 175 atoms/ns versus a rate close to zero without a field.

The initial decrease in oxygen adsorption rate, seen without an electric field, sets in at a later moment in time if an electric field is placed over the oxide layer. This can be explained by the extra downward force, which is the electric field, on each oxygen atom if it approaches the aluminium. Equation 2.14 shows the force to be proportional to the applied field strength and the charge of a particle. At a higher field strength this force will therefore be higher for the same charge. This higher force increases the kinetic energy of the oxygen atoms as can be seen in Figure 3.10. Although for all field strengths the kinetic energy of the oxygen atoms that are inserted in the simulation box is initially equal, a higher field strength, and with that a higher force on the oxygen atoms, leads to higher kinetic energy peaks.

Figure 3.10: Kinetic energy of first six oxygen atoms that enter the simulation box versus time for simulations with an aluminium slab and a deposition of oxygen atoms at 300 K and at different electric field strengths.

Without a field an oxygen atom might get repelled by oxygen atoms in the aluminium surface. The force from the electric field, and with that the higher kinetic energy of the atom, will cause oxygen atoms that landed in the aluminium surface to move further down in the aluminium surface.
plane, Figure 3.11, making it possible for new oxygen atoms to land at the surface. There is initially no driving force for the oxygen atoms to move to the second aluminium plane, but since the oxygen atoms will move further down in the first plane, the aluminium atoms will be pushed upwards. The electric field assists this both by a downward force on the oxygen and an upward force on the aluminium. Oxygen atoms that have moved further down in the surface plane can get more charge transferred from the aluminium, since there will be more aluminium atoms in their neighbourhood, Figure 3.12. Since the oxygen atoms have moved further down and aluminium has moved up, new arriving oxygen atoms will not be repelled by the adsorbed oxygen atoms, but will be attracted by the positively charged aluminium atoms and therefore be adsorbed in the oxide layer. A decrease in adsorption rate will thus set in at a later moment in time. Even though the electric field poses a force on the oxygen atoms in the oxide layer, at 300 K, for field strengths up to 1.5 V/Å, this force apparently is not high enough to facilitate the ion movement in the oxide layer in such a way that the adsorption rate is increased.

Initially, merely the aluminium surface plane is involved in the formation of aluminium oxide. Only occasionally an oxygen atom moves further down in the aluminium slab, creating a possibility for another oxygen atom to move down or an aluminium atom to move up resulting in an available surface site. The available number of surface sites however, is decreasing rapidly resulting in a large decrease in adsorption rate, as can be seen in Figure 3.7.
3.2.2 Influence of temperature

The influence of temperature on the adsorption rate can be seen if Figure 3.7a and 3.7b are compared. Raising the temperature from 300 K to 600 K has a similar effect as applying an electric field of 0.5 V/Å at 300 K. The initial decrease in oxidation rate sets in at a later moment in time. At a higher temperature the collision frequency of oxygen atoms with the aluminium surface, equation 3.1, and with that the frequency with which an atom is inserted in the simulation box, will be lower. The velocity of oxygen atoms approaching the surface however, will be higher. Their higher kinetic energy enables more oxygen atoms to overcome the barrier caused by repulsion by adsorbed oxygen atoms and actually get adsorbed at the aluminium surface then would be the case at a lower temperature. A second influence of a higher temperature is that the adsorbed oxygen atoms will more easily move further down in the surface plane and aluminium will move up more easily, as in the case of an applied electric field at lower temperature, since the diffusion is increased at a higher temperature. This leads to the same effects on the adsorption rate as described previously for an electric field.

3.2.3 Structure of oxide layer

Placing an electric field over the oxide layer not only influences the number of oxygen atoms that get adsorbed and therefore the thickness of the oxide layer, the resulting structure of the oxide layer will also be influenced. Figure 3.13 shows the distribution of oxygen atoms in the z-direction of the simulation box. Here again the three regimes regarding the field strength can be seen. For field strengths up to 1.5 V/Å at 300 K or 0.5 V/Å at 600 K, the lowest regime shows the number of oxygen atoms to be the highest at the middle of the oxide layer and lower towards the edges. In the second regime, a field strength of 2.0 V/Å at 300 K and 1.0 or 1.5 V/Å at 600 K, the upper part of the oxide layer is comparable to an oxide formed without a field. Lower in the oxide layer there will be less oxygen atoms. For the third regime, a field strength of 2.0 V/Å at 600 K, the oxygen distribution has a much longer ‘tail’ in to the aluminium. This indicates that, although a higher field strength and a higher temperature promote the formation of an oxide layer, they might negatively influence the structure of this oxide layer. To get a thick oxide layer with a homogeneous structure it is therefore necessary to find an optimum combination of these parameters.

![Figure 3.13: Distribution of oxygen atoms in the oxide layers formed at 300 and 600 K and at different electric field strengths in simulations with an aluminium slab and a deposition of oxygen atoms.](image)

The linear growth of the number of adsorbed oxygen atoms with respect to time after the first 100 ps of simulated time seen for a field strength of 2.0 V/Å at 300 K and for field strengths of 1.0,
1.5 and 2.0 V/Å at 600 K, Figures 3.7a and 3.7b, suggests the movement in the oxide layer to be determined by the field strength and not to be influenced by the amount of adsorbed oxygen and therefore the thickness of the oxide layer. The decrease in adsorption and growth rate at the end of the simulations with a field strength of 2.0 V/Å at 300 K and 1.0 and 1.5 V/Å at 600 K might indicate a new stage in the oxidation process. To get a clearer view on the oxidation behaviour from this point on, the simulation should last longer.

### 3.2.4 Displacement of atoms in oxide layer

The effect of the electric field on the displacement of aluminium and oxygen atoms in the oxide layer is shown in Figure 3.14 for the simulations at 600 K. At 300 K the effect of the electric field, as can be seen from Figures 3.7 and 3.9, is comparable but less pronounced. The standard deviation \( s \) of the z-position of the aluminium atoms originally belonging to the same plane, plotted in Figure 3.14, is calculated according to

\[
s = \left( \frac{1}{n} \sum_{i=1}^{n} (z_i - \bar{z})^2 \right)^{\frac{1}{2}},
\]

where \( \bar{z} = \frac{1}{n} \sum_{i=1}^{n} z_i \).

\( z \) is the data vector containing the z-positions of the atoms, and \( n \) is the number of aluminium atoms per plane.

The average z-position of aluminium atoms originally belonging to the same plane, Figures 3.14a, 3.14d, 3.14g, 3.14j and 3.14m, shows that the order of the planes is retained. The upper planes on average are shifted more upwards than the lower planes, which is explainable from the volume expansion of aluminium upon the formation of aluminium oxide given by the Pilling-Bedworth ratio, equation 1.1. Although the Pilling-Bedworth ratio is based on measurements of aluminium and aluminium oxide in an equilibrium state and in the simulations the oxide formation is still proceeding and not yet in a steady-state, it can be expected that there will be an expansion of volume upon formation of aluminium oxide. Since the simulations are performed on FCC aluminium which has a close packed structure, oxygen atoms can only fit in between the aluminium atoms if the volume expands.

Without an electric field being applied or with a relatively low field strength of 0.5 V/Å, the adsorption rate decreases to almost zero at the end of the simulation, Figure 3.7b. The standard deviation of the z-position of the atoms per aluminium plane then becomes constant too, Figures 3.14c and 3.14f.

With an electric field strength of 1.0 or 1.5 V/Å the adsorption rate shows a similar behaviour, Figure 3.7b. The standard deviation of the z-position of the atoms per aluminium plane is also comparable for these two field strengths, Figures 3.14i and 3.14l. From the shape of the standard deviation curves it can clearly be seen that the oxidation process of aluminium proceeds per aluminium plane.

The oxygen atoms that are at the lowest z-position at the end of the simulation, Figures 3.14b, 3.14e, 3.14h, 3.14k and 3.14n, are the oxygen atoms that entered the simulation box in the early stages of the simulation and therefore were adsorbed in the oxide layer early in the simulation.

Due to the non-perfect structure of the oxide layer during the formation of this layer, atoms can move inside the layer, assisted by the electric field. A vacancy in the structure can be filled by an atom, creating a new vacancy position, etcetera. This makes it possible for oxygen atoms to come at a lower position in the oxide layer and for aluminium atoms to move up. In the classical picture oxygen ions move through the oxide layer to react with aluminium at the metal/oxide interface, Figure 3.15a, or aluminium ions move through the layer to react with oxygen at the oxide/gas interface. Both these processes are not seen. Due to new oxygen entering the oxide layer, other oxygen ions are pushed down, leading to the lowest oxygen atoms moving even lower to react with
the aluminium at the metal/oxide interface, Figure 3.15b. The aluminium that reacts with oxygen at the oxide/gas interface is mostly aluminium from the top layer that has shifted upwards, as can be seen in Figure 3.16, where the aluminium atoms that originally belonged to the upper plane are shown in yellow.

For a field strength of 2.0 V/Å the displacements in the aluminium layers become so large, larger than the initial distance between aluminium planes which was 2.025 Å, that, although the average order of the planes is still retained, Figure 3.14m, the atoms from the different layers have changed places with respect to each other. The highest aluminium atoms at the end of the simulation are no longer mostly atoms from the first plane as can be seen in Figure 3.16e. The standard deviation of the z-position of the aluminium atoms per plane becomes much larger than for a lower field strength and keeps increasing at a higher rate than for a lower field strength, Figure 3.14o. The number of adsorbed atoms for this field strength also keeps increasing at a higher rate than for a lower field strength, Figure 3.7b. This field strength apparently makes it possible for the ions in the oxide layer to overcome a certain energy barrier, resulting in more ion movement, which leads to a much thicker oxide layer.

The charges predicted by ReaxFF for ions in the oxide layer, depend on the local environment of these ions. For the oxide layer grown at 300 K without an electric field, the charge distribution of ions inside the oxide layer at the end of the simulation is shown in Figure 3.17a. Only ions within boundaries determined by the average height of the five highest aluminium atoms and the average height of the five lowest oxygen atoms are included. From this figure it becomes clear that the charge distribution calculated by ReaxFF does not match the equilibrium charges in Al₂O₃, which would be +3 for aluminium and -2 for oxygen. In this oxide layer there are 53 aluminium atoms versus 50 oxygen atoms. At 300 K an amorphous layer is expected to grow. The actual ratio between aluminium and oxygen ions and with that the ratio between the charges will depend on the number of adsorbed oxygen atoms. However, the absolute charges calculated by ReaxFF are lower than those predicted by chemical theory and other potentials, as will be shown in section 7.3. Since the force posed on ions by the electric field is proportional to the charge of these ions, if a lower charge is calculated, a higher field strength needs to be applied to get the same force.

The results from the simulations described in this chapter and those described in the following chapters are summarized in Table 6.1.
Figure 3.14: Average z-position of aluminium atoms per (initial) plane, final z-position of oxygen atoms in oxide layer versus insertion time in simulation box, and standard deviation of z-positions of aluminium atoms per (initial) plane at 600 K and at different electric field strengths for simulations with an aluminium slab and a deposition of oxygen atoms.
(a) Classical picture of oxygen ion migration through oxide layer. An oxygen ion enters the oxide layer and migrates all the way through it until it reaches the aluminium surface and reacts there to form aluminium oxide.

(b) Oxygen ion migration in simulations. An oxygen ion entering the oxide layer pushes another oxygen ion downwards. This other oxygen ion will push yet another oxygen ion down, leading to a chain reaction of events, resulting eventually in an oxygen ion reaching the aluminium surface and reacting with the aluminium to form new aluminium oxide.

Figure 3.15: Oxygen ion migration in oxide layer in both classical picture and as seen in simulations.

(a) 0.0 V/Å  (b) 0.5 V/Å  (c) 1.0 V/Å  (d) 1.5 V/Å  (e) 2.0 V/Å

Figure 3.16: Final configurations for simulations with an aluminium slab and a deposition of oxygen atoms at 600 K and at different electric field strengths. Blue spheres represent aluminium, red spheres represent oxygen and yellow spheres represent the aluminium atoms that originally belonged to the upper plane.
Figure 3.17: Distribution of charges and ratio between oxygen and aluminium atoms in oxide layer grown at aluminium slab by a deposition of oxygen atoms at 300 K without an electric field applied. Only ions within boundaries determined by the average height of the five highest aluminium atoms and the average height of the five lowest oxygen atoms are included. Red spheres represent oxygen atoms, blue triangles represent aluminium atoms.
Chapter 4

Oxidation of aluminium in the presence of water under the influence of an electric field

Since anodizing is performed in aqueous solutions, the interaction between aluminium and water under the influence of an electric field is studied. Water is known to show self-dissociation according to

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]  \hspace{1cm} (4.1)

The equilibrium reached in this reaction depends on temperature and pressure. Pure water is neutral and the concentration of hydrogen ions, \([\text{H}^+]\), equals the concentration of hydroxide ions, \([\text{OH}^-]\). The pH of water, which is defined as \(-\log[\text{H}^+]\), equals 7 at room temperature and standard pressure. The concentration of both hydrogen and hydroxide ions therefore equals \(10^{-7}\) mol/liter. To have one hydroxide and one hydrogen ion in a simulation reflecting a pH of 7, the volume filled with water should measure \(1.7 \times 10^{10}\ \text{Å}^3\). Since this is unreasonable given the computational costs, one cannot expect any of the water molecules to be ionized in the actual simulations, which have a water volume of either \(8.6 \times 10^3\ \text{Å}^3\) or \(2.5 \times 10^4\ \text{Å}^3\).

If however, through dissociation of water at the aluminium surface, water dissociates and protons and hydroxyl groups are formed, these hydroxyl groups are expected to combine with water molecules and form hydronium ions:

\[ \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \]  \hspace{1cm} (4.2)

In this chapter the setup of the simulations will be described first. The results of the different simulations and the conclusions that can be drawn based on these results, regarding the influence of the applied electric field on the ion movement and dissociation of water molecules, are given next.

4.1 Setup of simulations with aluminium and water

The simulation box measures \(20.2 \times 20.2 \times 70.0\ \text{Å}^3\) and consists of 1000 aluminium atoms and 256 water molecules. It has periodic boundary conditions in x- and y-directions. In between the water and the aluminium is a vacuum created. The water molecules and the aluminium slab are first let to relax separately. To ensure the volume of water to stay constant during the relaxation, the region containing water is bounded by reflecting walls in the z-direction. The relaxation is performed at 300 K during 10 ps with a time step of 0.1 fs.

After relaxation, the water is brought close to the aluminium and above the water a reflecting wall is placed, to prevent atoms from leaving the simulation box. Simulations are performed at
300 K and electric field strengths of 0.0, 0.5, 1.0, 1.5 and 2.0 V/Å. Again the electric field is only defined over the oxide layer.

If water dissociates and an oxide layer starts to form, the amount of water modelled should be high enough to provide the oxygen needed for the formation of the oxide layer. The simulations are therefore repeated with the same aluminium slab and 788 water molecules. The simulation box measures 20.2 × 20.2 × 110 Å³. The aluminium and water are again first separately let to relax, before bringing the water close to the aluminium.

4.1.1 Simulations with dissociated water molecule

Although, as previously described, with the current size of the simulation box, the equilibrium number of hydrogen and hydroxyl ions is vanishingly small, it can be expected that the presence of ions in a larger system will influence the reactions at the aluminium surface. Therefore simulations are also performed in which one of the water molecules is forced in a dissociated state at the start of the simulation. To create a dissociated water molecule, after relaxation of the structure consisting of 1000 aluminium atoms and 256 water molecules, one of the hydrogen atoms of one of the 256 water molecules is displaced with respect to the hydroxyl group of the molecule. Since ReaxFF calculates the bond order depending on the bond distance, if the hydrogen atom is displaced far enough, there will no longer be a bond between the hydrogen atom and the hydroxyl group of the water molecule. The actual charges of the created ions will be calculated by ReaxFF and depend on the total distribution of atoms in the system. To prevent rapid recombination of the hydroxyl group and the hydrogen ion, the hydrogen ion is displaced towards the upper part of the simulation box, while the hydroxyl group is at approximately 2.5 Å above the aluminium surface. Simulations are performed for 1000 ps at 300 K and at electric field strengths of 0.0, 0.5, 1.0, 1.5 and 2.0 V/Å.

4.1.2 Simulations with vacancy in aluminium surface

At a perfect aluminium (100) surface the energy barrier for water to dissociate at the surface can be very high. In order for water to dissociate it should bond at the aluminium surface and one of the O-H bonds should be broken. The hydroxyl group will preferentially bind to two aluminium surface atoms [33], which leads to a disruption of the structure of the aluminium surface. The energy needed for the hydroxyl group to bind at two aluminium surface atoms and, with that, disrupt the structure of the aluminium surface is expected to depend on the initial structure of the aluminium surface layer. For a perfect crystal structure this energy is expected to be higher than for a less perfect structure. The presence of a vacancy in the aluminium surface layer might lower the energy barrier for the dissociation of a water molecule at this surface, and therefore promote the formation of an oxide layer. To investigate the influence of a vacancy in the aluminium surface, simulations are performed with the same aluminium slab of 1000 atoms and 256 water molecules. After relaxation of the structure, one of the atoms in the aluminium surface plane is removed and simulations are performed for 500 ps at 300 K with electric field strengths of 0.0, 0.5, 1.0, 1.5 and 2.0 V/Å.

4.1.3 Simulations with native oxide layer

Since an aluminium surface in practice will always be covered with a native oxide layer, also the interaction between water and an oxide layer is studied under the influence of an electric field. Three different situations are considered. A (100) aluminium surface covered with an oxide layer grown at 300 K, chapter 3, the same aluminium surface covered with an oxide layer grown at 600 K and a (111) aluminium surface covered with an oxide layer grown at 300 K and under an atomic oxygen density representing a pressure of 154 atm [30].

In the case of the (100) aluminium surface with the oxide layer grown at 300 K, the slab consists of 1000 aluminium atoms, there are 70 oxygen atoms in the oxide layer and 740 water molecules.
are modelled above the slab. The oxide layer grown at 600 K consists of 86 oxygen atoms. Here there are 742 water molecules modelled. The slab with the (111) aluminium surface consists of 483 aluminium atoms, there are 115 oxygen atoms in the oxide layer and there are 305 water molecules modelled above the slab, while the surface measures $22.8 \times 19.8 \, \text{Å}^2$. Simulations are performed for 1000 ps at 300 K with electric field strengths of 0.0, 1.0, 1.5, 1.7 and 2.0 V/Å.

### 4.1.4 Determination of oxide layer

At higher field strengths water not only reacts with the aluminium leading to the formation of an oxide layer, aluminium atoms can also dissolve in the water. Since the oxide layer was defined in between the highest aluminium atom and the lowest oxygen atom plus a cutoff value at both sides, as described in section 3.1, the dissolution of an aluminium atom in water would lead to a large increase in the calculated thickness of the oxide layer. The electric field is defined over the oxide layer, resulting in the field being placed over the solution if an aluminium atom is dissolved in it. The definition of the oxide layer is therefore modified, to account for aluminium dissolving in water. To define the upper boundary of the oxide layer, instead of determining the z-position of the highest aluminium atom, the z-position of the highest aluminium atom that can still be considered part of the oxide layer is determined.

An aluminium atom is considered to be part of the oxide layer if it has at least three aluminium neighbours within a certain cutoff value. This value is determined by analysis of the aluminium-aluminium distance in the oxide layers formed by a deposition of atoms at 300 K and different field strengths, chapter 3. In Figure 4.1 it can be seen that the distance between two neighbouring aluminium atoms is approximately 2.9 Å, if the aluminium atoms are next to each other, or 3.5 Å, if there is an oxygen atom in between the two aluminium atoms. The bond distance stays underneath 4.0 Å. The cutoff value for determining whether or not an aluminium atom is part of the oxide layer is therefore set at 4.0 Å.

![Figure 4.1: Distribution of aluminium-aluminium bonds in oxide layer formed at aluminium (100) surface at 300 K under the influence of atomic oxygen at different electric field strengths. The peak at 2.9 Å gives the bond length between two neighbouring aluminium atoms. The peak at 3.5 Å reflects the bond length between aluminium atoms with an oxygen atom in between them.](image-url)
4.2 Results of simulations with aluminium and water

4.2.1 Influence of water presence on oxidation

In Figure 4.2 the initial and final configurations are shown for the simulations with an aluminium slab of 1000 atoms and 256 water molecules. The simulations lasted 1000 ps without a field and with field strengths of 0.5 and 1.0 V/Å, and 200 ps for a field strength of 1.5 respectively 2.0 V/Å.

(a) initial configuration
(b) 0.0 V/Å, 1000 ps.
(c) 0.5 V/Å, 1000 ps.
(d) 1.0 V/Å, 1000 ps
(e) 1.5 V/Å, 200 ps.
(f) 2.0 V/Å, 200 ps.

Figure 4.2: Initial and final configurations for simulations with aluminium and 256 water molecules at 300 K and at different electric field strengths. The aluminium slab consists of 1000 aluminium atoms and is 20 layers high. For clarity only the upper part of the aluminium slab is shown. Blue spheres represent aluminium, red spheres represent oxygen and grey spheres represent hydrogen.

The thickness of the developing oxide layer for all field strengths is shown in Figure 4.3a. The number of oxygen atoms and aluminium atoms in the layer are shown in Figures 4.3b and 4.3c. Due to the definition of oxide thickness as explained in section 4.1.4, when the lower boundary of the oxide layer shifts downwards, a whole aluminium plane can be suddenly considered to be part of the oxide layer. This is shown in Figure 4.3c as a stepwise increase in the number of aluminium atoms in the oxide layer.

Without an electric field and with field strengths of 0.5 and 1.0 V/Å a layer of adsorbed water molecules forms, Figures 4.2b, 4.2c and 4.2d. The energy barrier for the dissociation of water at the aluminium surface apparently is too high for field strengths up to 1.0 V/Å. A higher field strength results in the formation of an oxide layer, Figures 4.2e and 4.2f. This oxide layer consists not, as in simulations with atomic oxygen, only of aluminium and oxygen. There are hydrogen atoms, hydroxyl groups and water molecules in the oxide layer as well. After 200 ps for every aluminium atom there are approximately 1.8 oxygen atoms and 3 hydrogen atoms in the oxide layer. Given the stepwise increase in the number of aluminium atoms considered to be part of the oxide layer, the ratio between aluminium and either hydrogen or oxygen atoms can vary substantially.

There is charge transferred between the adsorbed water molecules and the aluminium atoms from the surface plane. This results in a surface charge on the aluminium. The surface charge
Figure 4.3: Thickness of oxide layer and number of oxygen and aluminium atoms versus time in oxide layer for the first 200 ps of simulated time for simulations with aluminium and 256 water molecules at 300 K and at different electric field strengths.

is defined here as the average charge of the aluminium atoms in the upper aluminium plane. In Figure 4.4a the surface charge is shown for the simulations with a field strength of 0.0, 0.5, and 1.0 V/Å. From this figure it becomes clear that the field strength influences the surface charge. In Figure 4.4b the surface charge is shown for the first 10 ps of the simulations at all field strengths. When water dissociates at the surface and an oxide layer starts to form, the aluminium atoms that originally belonged to the upper plane will no longer form a surface of the aluminium and therefore the definition of surface charge loses its meaning.

Figure 4.4: Surface charge of aluminium in simulations with aluminium slab and 256 water molecules at 300 K and at different electric field strengths.

The distance between the adsorbed water layer and the aluminium surface for field strengths up to 1.0 V/Å is not substantially influenced by the field strength. A higher field strength will cause the aluminium surface plane to move down. As can be seen in Figure 4.5a not just the surface plane moves down but all upper planes are pushed downwards. Since the bottom plane is fixed and simulations are performed keeping the volume of the system constant, this means the aluminium structure becomes more dense as it is pushed together by the water molecules. The charges on the upper four aluminium planes as well as on the adsorbed water layer and the bulk water are shown in Figure 4.5b. From this figure it becomes clear that the charges on the first two aluminium planes are influenced by the presence of an electric field. The charge of the adsorbed water layer fluctuates more for a lower field strength, but on average is not substantially different than for a
field strength of 1.0 V/Å.

![Graph showing field strength vs. z-position and charge]  

(a) Average z-position per aluminium plane and water layer.  

![Graph showing charge vs. z-position and time]  

(b) Average charge per aluminium plane and water layer.  

![Graph showing difference in average z-position]  

(c) Difference in average z-position between hydrogen and oxygen atoms from water molecules in adsorbed water layer.

Figure 4.5: Charges and z-positions for simulations with an aluminium slab and 256 water molecules at 300 K and at different electric field strengths.

In the adsorbed water layer the water molecules are oriented more or less parallel to the aluminium surface. The hydrogen atoms have on average a slightly higher z-position than the oxygen atoms. In Figure 4.5c it can be seen that the average difference between the z-positions of oxygen and hydrogen atoms is influenced by the field strength. After the first 500 ps of the simulation with
a field strength of 1.0 V/Å a steady-state seems to be reached wherein the aluminium surface is completely covered with adsorbed water molecules on aluminium top sites. The same observation regarding the position and orientation of water molecules is made for the aluminium (100) and (111) surface and various other metals [34, 35, 36], in the absence of an electric field, based on DFT calculations and experiments.

The charge distribution, Figure 4.5b, shows the aluminium surface plane to be positively charged. The water is negatively charged, with those molecules that form the adsorbed layer more negatively charged than the bulk. The second aluminium plane gets a negative charge, slightly more negative than the charge from the adsorbed water. This charge distribution arises from the QEq procedure used to calculate the charges. This will be further explained in section 7.2.

Without an electric field there is a balance between the attraction of the aluminium atoms from the top plane towards the negatively charged adsorbed water layer and towards the negatively charged second aluminium plane. The aluminium planes therefore are not displaced. Upon applying an electric field, this balance is disrupted and the aluminium planes move down. Only a high enough electric field can overcome the energy barrier for dissociation of water molecules.

From an electric field of 1.5 V/Å on an oxide layer starts to form. In the simulations this does not always start with the dissociation of water. Due to the electric field aluminium can be pushed out of the surface plane before any water dissociates. This indicates that the field strength needed to enable dissociation of water is too high regarding the aluminium behaviour. Saitta et al. [37] have shown in an ab initio molecular dynamics study field strengths above 0.35 V/Å being able to dissociate water molecules.

Upon formation of the oxide layer it becomes clear that the amount of water modelled is important. During the formation of the oxide layer, all water molecules are attracted towards this oxide layer. The oxide layer consists not only of oxygen and aluminium and is not a dense layer as when formed under the influence of atomic oxygen. The layer has a very open structure and contains hydrogen atoms, hydroxyl groups and water molecules as well, Figures 4.2e and 4.2f. To provide enough oxygen for the formation of aluminium oxide much more water molecules are therefore needed than would be expected based on the structure of the oxide layer formed in oxygen gas. When water molecules dissociate at the oxide-water interface they form a hydroxyl group and a hydrogen atom. This hydrogen atom binds to a water molecule to form a hydronium ion. These hydronium ions, if in the region where the electric field acts, feel an upward force. At the end of the simulation with a high field strength a thick open structured oxide layer is formed, with above the oxide layer only hydronium ions left, indicating that not enough water is modelled.

To account for the amount of oxygen needed at high field strengths for the formation of the oxide layer, simulations are performed with 788 instead of 256 water molecules and a field strength of 1.5 and 2.0 V/Å. The resulting thickness and number of aluminium and oxygen atoms are shown in Figure 4.6.

From this figure it can be seen that the amount of water modelled is not only important for the reasons described above, but the amount of water modelled also determines whether or not an oxide layer is formed at all. In the simulation with a field strength of 1.5 V/Å and a small amount of water, the oxide layer started to form at the beginning of the simulation, while with a large amount of water formed, almost no oxidation occurs. With a field strength of 2.0 V/Å oxidation does occur, but it takes 100 ps before it sets in. The influence the amount of water has on the modelling of the oxidation process can be explained by the different charge distribution calculated by ReaxFF for a different amount of water molecules. In all simulations with an aluminium slab and water, initially the total charge calculated on the aluminium is positive, while the total charge of the water is negative. The exact values of the charges depend on the number and distribution of atoms. In the simulation with 788 water molecules the average initial charge per water molecule was half of the initial charge per water molecule in the simulation with 256 water molecules, while the charges on the first two aluminium planes were also lower. During the simulations not the average charges but the charges on individual aluminium atoms and water molecules determine the attraction between...
them and the force working on them by the electric field. Only certain water molecules dissociate at the aluminium surface indicating that only a specific combination of orientation, charge, and field strength makes it possible for water molecules to overcome the energy barrier for dissociation. A different charge distribution will influence the probability for this specific combination of factors to occur and with this the dissociation probability of water molecules and oxidation behaviour of aluminium.

The composition of the oxide layer formed at 2.0 V/Å changes with time. As can be seen in Figure 4.7 after 300 ps the same proportion between the number of aluminium, oxygen and hydrogen atoms is reached as in the oxide layers formed at 1.5 and 2.0 V/Å with 256 water molecules in the simulation box. After this time the ratio between oxygen and aluminium atoms and the ratio between hydrogen and aluminium atoms decreases, while the ratio between hydrogen and oxygen atoms shows only a very slight decrease. In Figures 4.6b and 4.6c it can be seen that the adsorption rate of oxygen atoms decreases more than the rate with which aluminium atoms become part of the oxide layer. This is reflected in Figure 4.7 as a decrease in the ratio between oxygen and aluminium atoms.

Figure 4.7: The ratio between respectively oxygen and aluminium atoms, hydrogen and aluminium atoms, and hydrogen and oxygen atoms versus time, in the simulation with an aluminium slab and 788 water molecules at 2.0 V/Å and 300 K.

The oxide layer grown in the first 300 ps consists of a considerable number of water molecules.
These water molecules dissociate, forming hydrogen ions and hydroxyl groups, which in turn can dissociate into hydrogen ions and oxygen ions. Although in the first 300 ps of the simulation water is seen to dissociate and in the second part of the simulation water molecules are adsorbed in the oxide layer, at 300 ps a turning point is seen where the dissociation of water to form new oxide, leading to an increase in aluminium atoms in the oxide layer, becomes more important than the adsorption of water molecules. At the end of the simulation at 1000 ps the resulting oxide layer has an open structure, Figure 4.8, and consists of aluminium and oxygen atoms and water molecules, hydroxyl groups and hydrogen ions. A continuation of this process, in which the dissociation of water is more important than the adsorption of water molecules, might eventually lead to a more dense oxide layer consisting mainly of aluminium and oxygen.

![Figure 4.8: Oxide layer at 1000 ps formed in a simulation with an aluminium slab and 788 water molecules at 2.0 V/Å and 300 K. Blue spheres represent aluminium, red spheres represent oxygen and grey spheres represent hydrogen.](image)

**4.2.2 Influence of ions in solution**

The initial and final configurations for the simulations performed with water molecules and an aluminium slab in which one of the water molecules was dissociated at the start of the simulation, are shown in Figure 4.9. The hydroxyl group, resulting from the dissociation of one water molecule, binds within the first two picoseconds at a bridge position at the aluminium surface. Charge is transferred between the hydroxyl group and the surrounding aluminium atoms. One of these aluminium atoms then moves out of the surface plane. The hydroxyl group is dissociated into an oxygen atom and a hydrogen atom. Without an electric field being applied, at the end of the simulation, this oxygen atom is at a position between three aluminium atoms with one of these aluminium atoms sticking out of the surface plane. This is the only difference seen compared with the simulation in which all water molecules were complete at the start of the simulation. Above the remaining aluminium surface an adsorbed water layer forms.

The resulting thickness of the oxide layer and the number of oxygen and aluminium atoms in this layer are shown for all field strengths in Figure 4.10. By comparing Figure 4.9 and Figure 4.10 it can be seen that, although for lower field strengths the presence of ions in the solution leads to
some activity at the aluminium surface, a field strength of at least 1.5 V/Å is needed for the actual formation of an oxide layer within the simulated time. This is the same field strength as the field strength needed for the formation of an oxide layer without ions being present initially.

4.2.3 Influence of vacancy in the aluminium surface layer

With a vacancy in the aluminium surface plane, the oxidation behaviour is not significantly influenced. Just as with a perfect crystal an adsorbed water layer forms for field strengths up to 1.0 V/Å. For higher field strengths an oxide layer starts to form as can be seen in Figure 4.11. During the formation of the adsorbed water layer at low field strengths, water molecules above the vacancy come at a lower position, due to the missing aluminium atom at that surface site. Eventually the adsorbed water layer is not different than that formed above a perfect surface, as can be seen in Figure 4.12. Apparently the regular structure of the adsorbed layer is energetically more favorable for a water molecule than it is to move out of that layer and be adsorbed or dissociated at the vacancy position.

The results obtained with a vacancy in the aluminium surface plane are comparable with the results obtained if starting with ions in the solution. In both cases, even though there might be some surface activity, the formation of an adsorbed water layer is clearly energetically the most favourable for field strengths up to 1.0 V/Å.

4.2.4 Influence of native oxide layer

In the simulations with water and a native oxide layer on top of the aluminium surface, this native oxide layer is grown without an applied electric field. Oxide layers grown at 300 and 600 K are
used, that were grown for 1000 ps, as explained in chapter 3. The adsorption rate after 1000 ps was close to zero and at this time there was no movement from ions in the oxide layer other than the normal vibrations. Two things were expected in the current simulations. Placing an electric field over these oxide layers could cause displacements in the oxide layer. At the same time an interaction with the water molecules is expected, which could cause displacement in the oxide layer and adsorption of new atoms. This will now be investigated.

The initial and final structures after 1000 ps of simulated time for different field strengths are shown in Figure 4.13 for the oxide layer formed at 300 K on the (100) aluminium surface. At the start of the simulations the outermost layer of the oxide consists of oxygen. This gives the oxide a negative surface charge. For the oxide layer to grow, new oxygen atoms have to be adsorbed in the oxide layer. The negatively charged oxygen atoms in the water however, will be repelled by the negatively charged oxygen atoms at the oxide surface. The positively charged hydrogen atoms in the water will be attracted by the negatively charged oxygen atoms at the oxide surface. From the simulation without an electric field applied, it can be seen, Figure 4.13b, that this leads to dissociation of water molecules. One of the hydrogen atoms binds to an oxygen atom at the oxide surface and the hydroxyl group moves back into the water. From the fact that not all the oxygen atoms of the oxide surface are bonded to a hydrogen atom at the end of the simulation, it can be concluded that the necessary conditions for this process to occur are not always met. The charge of the oxygen atom from the oxide layer, the orientation of both the oxygen atom and the water molecule, and the charge distribution in the water molecule due to interaction with other water
molecules are all factors that can influence the dissociation behaviour of a water molecule at the oxide surface.

The final configurations shown in Figure 4.13 and the resulting number of oxygen atoms in the oxide layer for all three native oxide layers and all field strengths, Figure 4.14, show that applying an electric field leads to adsorption of oxygen in the oxide layer. Applying an electric field over the oxide layer means exerting a force on the ions in this layer. These ions feel a force proportional to their charge. If this force is high enough it can make the positively charged aluminium ions move up and the negatively charged oxygen ions move down. The positively charged aluminium atoms that end up at the oxide/water interface can attract negatively charged oxygen atoms from the water or the hydroxyl groups formed upon dissociation of water. These water molecules or hydroxyl groups can dissociate, leading to more oxygen atoms in the oxide layer and therefore actual growth of the oxide layer. The field strength influences both the ion movement in the oxide layer, as was shown in chapter 3, and the dissociation of water molecules, as can be seen in section 4.2.

In Figure 4.15 the difference in average z-displacement of aluminium and oxygen ions belonging to the native oxide layer is shown for all field strengths. Without an electric field being applied this difference is approximately zero, indicating that there is no movement in the oxide layer. Since the outer surface of the oxide was already covered with oxygen, no more oxygen can be adsorbed.

With an electric field applied, the difference in z-displacement between oxygen and aluminium ions in the oxide layer shows a large increase in the first 10 ps and a more gradual increase in the remaining simulated time. The number of adsorbed oxygen atoms in the oxide layer, Figure 4.14, shows the same behaviour. In chapter 3 it was shown that at 300 K a field strength of 2.0 V/Å leads to a much larger number of adsorbed oxygen atoms and a thicker oxide layer than a lower field strength does. In the simulations with aluminium covered with a native oxide layer and water this influence of the field strength can not be seen. For all field strengths the adsorption rate approaches zero at the end of the simulation, Figure 4.14. The dissociation of water can therefore be indicated as the rate determining step in the oxidation process. After the initial rearrangements have taken place in the oxide layer, if no new oxygen enters the oxide layer, by dissociation of water molecules, there is no driving force for ion movement anymore.

In the case of the native oxide layer grown at the (100) surface at 300 K or 600 K, an applied
Figure 4.13: Initial and final configurations for simulations with aluminium covered with a native oxide layer formed at 300 K on (100) aluminium, and water at 300 K and with different electric field strengths. The original aluminium slab consisted of 1000 aluminium atoms and was 20 layers high. For clarity only the upper part of the aluminium slab is shown. The native oxide layer consists of 70 oxygen atoms. Blue spheres represent aluminium, red spheres represent oxygen and grey spheres represent hydrogen.

Field of at least 1.7 V/Å is needed to get dissociation of a hydroxyl group into oxygen and hydrogen. With a field strength of 1.7 V/Å one hydroxyl group has dissociated and this resulted in a new oxygen atom inside the oxide layer bonded to three aluminium atoms. A field strength of 2.0 V/Å leads to more dissociated hydroxyl groups and therefore more new adsorbed oxygen atoms inside the oxide layer. With field strengths of 1.0 or 1.5 V/Å all new adsorbed oxygen atoms at the surface of the oxide layer are still part of a water molecule or hydroxyl group.

The native oxide layer grown at the (111) surface at 300 K was grown under a higher oxygen pressure than the native oxide layers grown at the (100) surface and therefore, even though it had grown for only 500 ps, there are relatively more oxygen atoms in the oxide layer than in the layers grown at the (100) surface. The initial and final number of oxygen atoms per Å$^2$ are given in Table 4.1 for all three native oxide layers for a field strength of 2.0 V/Å. Even with a field strength of 2.0 V/Å all new adsorbed oxygen atoms in the simulation with the native oxide layer grown at the (111) surface are still part of a hydroxyl group and are not adsorbed in the oxide layer as single oxygen atoms. From Figure 4.14 and Table 4.1 it can be seen that the composition of the native oxide layer influences the adsorption of oxygen during anodizing.

As already mentioned in section 4.2.1, the dissociation of water seems to be not properly described by ReaxFF. With a bare aluminium surface the electric field strength needed to start the formation of an oxide layer is very high. If the aluminium is covered with a native oxide layer at the start of the simulation, dissociation of water into a proton and a hydroxyl group occurs initially at all field strengths. The dissociation of those hydroxyl groups into a proton and a oxygen ion however, as is needed for the formation of an oxide layer, occurs only incidentally at the highest field strengths. With a native oxide layer the oxidation process has stopped at the end of the
(a) Native oxide layer grown at (100) surface at 300 K.  
(b) Native oxide layer grown at (100) surface at 600 K.  
(c) Native oxide layer grown at (111) surface at 300 K.

Figure 4.14: Number of adsorbed oxygen atoms in oxide layer for simulations with aluminium covered with a native oxide layer and water at 300 K and at different electric field strengths.

(a) Native oxide layer grown at (100) surface at 300 K.  
(b) Native oxide layer grown at (100) surface at 600 K.  
(c) Native oxide layer grown at (111) surface at 300 K.

Figure 4.15: Difference in average z-displacement between aluminium and oxygen atoms belonging to the native oxide layer for simulations with aluminium covered with a native oxide layer and water at 300 K and at different electric field strengths.

Table 4.1: Initial and final number of oxygen atoms in oxide layer per Å$^2$ after 1000 ps at 300 K and 2 V/Å for simulations with aluminium covered with a native oxide layer and water.

<table>
<thead>
<tr>
<th>Surface</th>
<th>300 K</th>
<th>600 K</th>
<th>300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.17</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>Final</td>
<td>0.28</td>
<td>0.33</td>
<td>0.33</td>
</tr>
</tbody>
</table>

In Table 6.1 the results of the simulations described in this chapter and those described in the previous and following chapters are summarized.
Chapter 5

Anodizing in the presence of oxalic acid

Depending on the process conditions aluminium when anodized in a strong acid solution can form a porous anodic alumina layer. A typical acid used in this anodization process is oxalic acid, Figure 5.1.

![Figure 5.1: Schematic representation of an oxalic acid molecule.](image)

An acid HA dissociates in water according to

\[ \text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \]  
(5.1)

The equilibrium constant for this reaction is the dissociation constant \( K_a \),

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]  
(5.2)

The \( pK_a \),

\[ pK_a = -\log K_a \]  
(5.3)

is the value used to describe the strength of an acid. A lower \( pK_a \)-value means a stronger acid. The dissociation of oxalic acid, \( \text{H}_2\text{C}_2\text{O}_4 \), takes place in two steps. The first step,

\[ \text{H}_2\text{A} \leftrightarrow \text{HA}^- + \text{H}^+ \]  
(5.4)

has a \( pK_a \) of 1.25 at 298 K. The second step,

\[ \text{HA}^- \leftrightarrow \text{A}^{2-} + \text{H}^+ \]  
(5.5)

has a \( pK_a \) of 3.81 [38].

To determine the influence of the presence of oxalic acid on the anodization behaviour of aluminium, simulations are performed with an aluminium slab and oxalic acid molecules dissolved in water. In this chapter the setup of these simulations is described first. Then the reactions at the aluminium/electrolyte or alumina/electrolyte interface are studied and the effect of the electric field on these reactions is determined.
5.1 Setup of simulations

To model an oxalic acid solution the same model as in the simulations with water, consisting of 1000 aluminium atoms and 788 water molecules, is used. In order to get a 10 wt% acid solution, 79 water molecules are removed and replaced with 16 oxalic acid molecules. This equals a concentration of 1.1 M. With a $pK_a$ for equation 5.4 of 1.25, the concentration of both $H^+$ and $OH^-$ should equal 0.25 M according to equation 5.2. Since the concentration of $H_2O$ diminishes substantially, this should be accounted for in calculating $[HA^-]$ and $[H^+]$. Therefore 0.22 M is a better approximation for these concentrations.

The $pK_a$ for the second dissociation step, equation 5.5, equals 4.19. This will not make a substantial contribution to the concentration of $H^+$ in the solution. For the volume used in the simulations this means there should be approximately 3 $H^+$-ions and 3 $HA^-$-ions in the simulation box.

5.1.1 Simulations with and without ions in solution

To investigate how the reactions are influenced by the ion concentration, simulations are performed both without starting with ions and starting with 5 dissociated acid molecules. In order to influence the exact ion concentration at the start of the actual simulation with or without an electric field, the relaxation of the structure is performed with complete acid molecules. After relaxation, the acid molecules are manually dissociated by displacing one of the hydrogen atoms of the molecules, resulting in the dissociation reaction given by equation 5.4. Since ReaxFF calculates the bond order depending on the distance between atoms, this will result in a hydrogen atom not bonded, thus dissociated, to the rest of the acid molecule. The charges on each atom are calculated every time step. The actual charge on the acid and hydrogen ion will depend on the total distribution of atoms in the simulation box, as described earlier in section 2.3. After relaxation of the structure and dissociation of the acid molecules, simulations are performed at 300 K with electric field strengths of 0.0, 1.0, 1.5, 1.7 and 2.0 V/Å lasting 1000 ps.

5.1.2 Simulations with native oxide layer

Since in practice an aluminium surface will always be covered with an oxide layer, simulations are performed with aluminium covered with a native oxide layer. The aluminium slab with an oxide layer grown on top of the (100) surface, from the simulation with atomic oxygen at 300 K without an electric field, chapter 3, is used again in these simulations. Since reactions are expected to be much slower than without an oxide layer, only 500 aluminium atoms are modelled to reduce the time needed to perform the simulations. There are 70 oxygen molecules in the oxide layer. Above the aluminium a solution of 666 water molecules and 15 oxalic acid molecules is modelled. This represents a 10 wt% oxalic acid solution. The unit cell measures $20.6 \times 20.6 \times 89.8 \text{ Å}^3$. Both the aluminium and the acid solution are let to relax during 10 ps.

Simulations are performed at 300 K with electric field strengths of 0.0, 1.0, 1.5, 1.7 and 2.0 Å. To study the influence of ions in the solution, simulations are performed both starting with complete acid molecules and with five acid molecules dissociated at the start of the simulation.

5.2 Results of simulations with oxalic acid molecules dissolved in water

5.2.1 Influence of presence of oxalic acid molecules on anodization of aluminium

The initial configuration and the final configurations after 1000 ps of simulated time for the simulations with a bare aluminium surface and an oxalic acid solution with initially complete oxalic acid molecules, are shown in Figure 5.2. From this figure it becomes clear that only a high enough
field strength leads to the formation of an oxide layer, just as in the case of pure water, section 4.2.1.

Figure 5.2: Initial and final configurations for simulations with a bare aluminium surface and an oxalic acid solution, consisting of 16 complete oxalic acid molecules and 709 water molecules, at 300 K and at different electric field strengths. The original aluminium slab consisted of 1000 aluminium atoms and was 20 layers high. For clarity only the upper part of the aluminium slab is shown. Blue spheres represent aluminium, red spheres represent oxygen, green spheres represent carbon and grey spheres represent hydrogen.

Without an external electric field being applied or with a field strength of 1.0 V/Å, just as in the simulation with pure water, an adsorbed water layer forms at the aluminium surface. All oxalic acid molecules, that were not dissociated at the start of the simulation, are still complete at the end of the simulation.

A field strength of 1.5 V/Å initially gives the same behaviour at the aluminium-electrolyte interface as with a lower field strength. An adsorbed water layer forms at the aluminium surface. After 650 ps of simulated time one adsorbed water molecule dissociates to form an adsorbed hydroxyl group and a hydrogen atom that moves back in the solution. This hydrogen atom binds not at a water molecule to form a hydronium ion, as seen in the simulations with pure water, instead it binds to one of the double bonded oxygen atoms of an oxalic acid molecule.

With field strengths of 1.7 and 2.0 V/Å the oxidation process starts with the dissociation of water molecules. The free hydrogen atoms that result from this dissociation bind to oxalic acid molecules. As the oxidation process proceeds these acid molecules are seen to bind at the aluminium surface themselves and dissociate, losing all of their hydrogen atoms and one or two oxygen atoms as they become part of the oxide layer.

The average z-position per aluminium layer and adsorbed water layer and the average charge of each layer are shown in Figure 5.3 for field strengths of 0.0, 1.0 and 1.5 V/Å. The same behaviour is seen as in the simulations with pure water and a bare aluminium surface. If an electric field is applied, when the water moves down to get adsorbed at the aluminium surface, it pushes the aluminium downwards, as explained in section 4.2.1. This behaviour results from the charge
distribution calculated by the QEq-procedure.

![Graph](image)

(a) Average z-position per layer.

![Graph](image)

(b) Average charge per layer

Figure 5.3: Average z-position and charge per aluminium and water layer for simulations with aluminium and an oxalic acid solution, consisting of 16 complete oxalic acid molecules and 709 water molecules, at 300 K and at electric field strengths of 0.0, 1.0 and 1.5 V/Å.

5.2.2 Influence of ions in solution

In Figure 5.4 the final configurations are shown for two simulations in which initially five oxalic acid molecules were dissociated. Without a field being applied the results is the same as without initially dissociated acid molecules. At the end of the simulation all single hydrogen atoms are bonded again to an oxalic acid molecule and an adsorbed water layer has formed at the aluminium surface. With a field strength of 1.5 V/Å however, an oxide layer starts to form.

As already mentioned in section 5.2.1 hydrogen atoms bind to the double bonded oxygen atom of complete oxalic acid molecules. Although unexpected if equations 5.4 and 5.5 are considered, the fact that hydrogen binds to the oxalic acid molecules can be explained if the charges that ReaxFF calculates for these molecules are considered. All oxalic acid molecules have a total charge of around -0.7, while the charge of the water molecules fluctuates around zero. If instead of starting with complete acid molecules, five of the acid molecules are dissociated at the start of the simulation, this hardly effects the average charges of all acid molecules together. The dissociated molecules have a slightly more negative charge while the hydrogen atoms have a slightly positive charge. The total charge of the two fragments of the molecule together is the same as for undissociated acid molecules.
Figure 5.4: Final configurations for simulations with a bare aluminium surface and an oxalic acid solution, consisting of 16 oxalic acid molecules and 709 water molecules, at 300 K and at different field strengths. Five of the oxalic acid molecules were dissociated at the start of the simulation. The original aluminium slab consisted of 1000 aluminium atoms and was 20 layers high. For clarity only the upper part of the aluminium slab is shown. Blue spheres represent aluminium, red spheres represent oxygen, green spheres represent carbon and grey spheres represent hydrogen.

If the charge on an oxalic acid molecule in water, without aluminium being present, is compared for different system sizes, it turns out that not the amount of water, but the general presence of water is influencing the charge of the oxalic acid molecule. For a cubic simulation box of $10 \times 10 \times 10 \text{Å}^3$ filled with 1 oxalic acid molecule and 28 water molecules, representing a density of 1 g/cm$^3$, the charge on the oxalic acid molecule after relaxation of the system during 1 ps at 300 K with a time step of 0.1 fs, is -0.5005. For a system of $20 \times 20 \times 20 \text{Å}^3$ filled with 1 oxalic acid molecule and 260 water molecules to have the same density, the charge on the oxalic acid molecule after relaxation is -0.5074. The charges are thus comparable, but since the molecule has not dissociated, the charge has a non-realistic value.

5.2.3 Influence of native oxide layer on anodization in oxalic acid solution

With a native oxide layer on the aluminium the same trends are seen as with pure water and a native oxide layer. Without an electric field applied, no new oxygen enters the oxide layer and the thickness of the layer remains constant. With an electric field applied, water molecules or hydroxyl groups bind at the aluminium, leading to an increase in thickness. The resulting number of adsorbed oxygen atoms in the oxide layer is shown in Figure 5.5 for both the simulations in which all oxalic acid molecules were complete at the start of the simulation and for the simulations in which five of the molecules were dissociated at the start of the simulation.

Although the number of adsorbed oxygen atoms seems to keep rising in Figure 5.5b for a field strength of 2.0 V/Å, this does not mean that there is more ion movement in the oxide layer and that there are actually more oxygen ions adsorbed in the oxide layer. The oxide layer at this field strength is seen to partly detach from the aluminium slab. The surface of the oxide becomes therefore higher at those parts where the oxide layer detached from the aluminium than at the parts where it is still connected to the aluminium slab. Since the thickness is calculated as the difference between the average $z$-position of the five lowest oxygen atoms and the average $z$-position of the five highest aluminium atoms that are still part of the oxide layer, if the surface becomes higher in one position, oxygen atoms from water molecules not adsorbed at the surface but above a lower surface position are taken into account when calculating the thickness of the oxide layer. To determine the real number of oxygen atoms in the oxide layer, the procedure to determine this number should be slightly altered.

The fact that the oxide layer detached from the aluminium slab in an oxalic acid environment and not in water can be explained by the presence of negatively charged oxalic acid molecules, as
calculated by ReaxFF, and ions. The aluminium ions in the oxide layer, apart from the upward force they feel from the electric field, feel an attraction towards these negatively charged molecules and ions. Although the negatively charged oxalic acid molecules feel a downward force, due to the electric field, if they are in the region where the electric field is applied, and due to attraction towards the positively charged aluminium, the force on the aluminium ions will be higher, since they have a higher absolute charge. Apparently the total force on the aluminium ions is high enough at an electric field strength of 2.0 V/Å to lead to detachment of the oxide layer.

The free hydrogen atoms that result from dissociation of water, just as without an oxide layer, prefer to bind to an acid molecule, since this is negatively charged while the water molecules have a charge close to zero. The average charge of the complete oxalic acid molecules is -0.6 versus -0.7 with a bare aluminium surface, while in both cases they are expected to be neutral.

### 5.3 Validity of simulations with oxalic acid

ReaxFF calculates a negative charge for an oxalic acid molecule dissolved in water. The value of this charge depends on the presence and distribution of other atoms in the simulation. Starting with a bare aluminium surface and oxalic acid molecules in water the charge on these molecules on average is -0.7, starting with aluminium covered with a native oxide layer and oxalic acid molecules in water the average charge on the oxalic acid molecules is -0.6 and placing one oxalic acid molecule in a simulation box filled with water leads to a charge on the oxalic acid molecule of -0.5. In all situations a complete oxalic acid molecule is supposed to be neutral. The reactions that take place during the simulations are influenced by this charge. The results from the simulations with oxalic acid can therefore not be valued as representative for anodization of aluminium in an oxalic acid solution.

In order to obtain more realistic results regarding the behaviour of oxalic acid, the employed parameterization of ReaxFF has to be re-fitted. The parameterization for aluminium, oxygen, hydrogen, carbon and nitrogen used in this study [28] is based on the parameterization for aluminium, oxygen and hydrogen [27] and a parameterization for carbon, hydrogen, oxygen and nitrogen [39]. The former is trained to correctly describe the interaction between aluminium and water, while the latter is trained to correctly capture the behaviour of glycine. In combining these two parameterizations additional fitting for the aluminium-nitrogen interactions is performed to correctly describe
the behaviour at the alumina/epoxy interface [28]. Although highly desirable, configurations of
the elements that are not included in the training of the force field will not always be properly
described. Unfortunately, for oxalic acid molecules this is the case.

Although an improved description of the ReaxFF parameterization will result in more realistic
charges for the oxalic acid molecule, it will not change the fact that the charge is dependent on
the total composition of the simulation box. The dependence of the charge of the oxalic acid
molecule on the environment, being either water, water above an aluminium slab or water above
an aluminium slab covered with a native oxide layer, is caused by the QEq-procedure to determine
the charges. This will be further explained in section 7.2.

The results from the simulations described in this chapter and the other simulations performed,
are summarized in Table 6.1.
Chapter 6

Anodizing aluminium in an ammonium tartrate solution

A weak acid used to grow a barrier coating in the anodization practice is ammonium tartrate, Figure 6.1. If ammonium tartrate dissolves in water it will dissociate in two ammonium ions and a tartrate ion. To study the influence of this acid on the initial oxidation steps under the influence of an electric field, simulations are performed with ammonium tartrate dissolved in water.

Figure 6.1: Schematic representation of ammonium tartrate.

First the setup of these simulations will be described. The effect of the presence of ammonium tartrate on the anodization behaviour of aluminium is described next, as well as the influence of the electric field on the reactions seen at the aluminium/electrolyte and alumina/electrolyte interface.

6.1 Setup of simulations

6.1.1 Simulations with a bare aluminium surface

The same aluminium slab as in the simulations with oxygen is modelled, chapter 3, containing 1000 atoms with the (100) surface facing upward, and above the aluminium ammonium tartrate dissolved in water is placed. In order to model a 20 wt% solution, 158 from the 788 water molecules are removed and replaced with 15 ammonium tartrate molecules.

After relaxation of the structure, as described in section 3.1, the acid solution is brought close to the aluminium and walls are placed to prevent atoms from leaving the simulation box. The ammonium tartrate molecules are placed in a dissociated form in the simulation box. Simulations are performed at 300 K and electric field strengths of 0.0, 1.0, 1.5, 1.7 and 2.0 V/Å.

6.1.2 Simulation with native oxide layer

In reality an aluminium surface will always be covered with an oxide layer. The effect of this native oxide layer on the anodization of aluminium in an ammonium tartrate solution is investigated by performing simulations in which an aluminium slab is modelled covered with a native oxide
layer. The aluminium slab with a native oxide layer from the simulation with atomic oxygen at 300 K without an electric field applied, chapter 3, is used in these simulations. To reduce the computational time needed to perform the simulations, only 500 aluminium atoms are modelled. There are 70 oxygen molecules in the oxide layer. Above the aluminium a solution of 592 water molecules and 14 dissociated ammonium tartrate molecules is modelled. This represents a 20 wt% ammonium tartrate solution. The unit cell measures $20.6 \times 20.6 \times 89.8$ Å$^3$. Both the aluminium and the solution are let to relax during 10 ps, before bringing the solution close to the aluminium and performing the actual simulations. These simulations are performed at 300 K and with electric field strengths of 0.0, 1.0, 1.5, 1.7 and 2.0 V/Å.

### 6.2 Results of simulations with aluminium and an ammonium tartrate solution

#### 6.2.1 Influence of tartaric acid on anodization of aluminium

The initial and final configurations of the simulations with a bare aluminium surface and ammonium tartrate dissolved in water are shown in Figure 6.2. Without an electric field being applied, an adsorbed water layer forms, just as with pure water or an oxalic acid solution. A field strength of 1.0 V/Å or higher however, leads already to the formation of an oxide layer. With pure water a field strength of 1.5 V/Å was needed for the formation of an oxide layer.

![Figure 6.2: Initial and final configurations for simulations with a bare aluminium surface and an ammonium tartrate solution at 300 K and at different electric field strengths. The original aluminium slab consisted of 1000 aluminium atoms and was 20 layers high. For clarity only the upper part of the aluminium slab is shown. Blue spheres represent aluminium, red spheres represent oxygen, green spheres represent carbon, small blue spheres represent nitrogen and grey spheres represent hydrogen.](image)

In contrast to the oxalic ion or molecule, the tartaric ion binds at the aluminium surface, resulting in charge transfer between the aluminium and the oxygen atoms. The resulting positively
charged aluminium atom can move out of the surface layer due to the force posed on it by the electric field. Since the regular structure of the surface layer is disrupted and the surface charge rises, water molecules can get adsorbed at the surface easier and dissociate. As can be seen from Figure 6.2b without an electric field acting on the interface between aluminium and the electrolyte, the regular surface structure is disrupted by the adsorption of a tartaric ion. This gives the opportunity for water molecules to dissociate at the surface, which leads to the movement of one aluminium atom out of the surface layer. A layer of adsorbed water molecules still forms, and no further activity is seen at the surface. The same effect was seen in simulations with aluminium and water, in which either one of the water molecules was dissociated at the start of the simulation, section 4.2.2, or a vacancy was present in the aluminium surface layer, section 4.2.3. The presence of an electric field is needed for the formation of an oxide layer in the timescale used in the simulations. The resulting thickness of the oxide layer and the number of oxygen and aluminium atoms in this oxide layer are shown in Figure 6.3.

In the simulations with atomic oxygen, chapter 3, it was shown that applying a field of 2.0 V/Å has a significant influence on the adsorption of oxygen in the aluminium surface, Figure 3.7a. With a solution of ammonium tartrate the same effect can be seen. Applying an electric field of 2.0 V/Å greatly enhances the adsorption of oxygen in the oxide layer. In water or an electrolyte however, not only the ion movement in the oxide layer determines the oxidation rate, the dissociation of water determines if there is oxygen available to form an oxide layer. From a field strength of 1.0 V/Å on water dissociates and an oxide layer starts to form. With a field strength of 1.0 V/Å initially a tartaric ion binds at the surface and an adsorbed water layer forms just as without a field being applied. Only after 200 ps of simulated time aluminium atoms move out of the surface layer, creating dissociation sites for water molecules, and an oxide layer starts to form. The rate with which this layer forms is then identical as for a field of 1.7 V/Å being applied, Figure 6.3b. This indicates that the electric field assists the oxidation by creating the possibility for water dissociation. The actual growth of the layer is then independent of the field strength, unless the field strength becomes so high that it can assist the ions in the oxide layer to overcome a certain energy barrier and the growth rate is enhanced. This is seen for a field strength of 2.0 V/Å.

**Orientation of tartrate ion**

The tartrate ions in the solution consist of a chain of four carbon atoms, as can be seen in Figure 6.1. The outer two carbon atoms are bonded to two oxygen atoms, a carboxylate group, while the inner two carbon atoms are bonded to a hydrogen atom and a hydroxyl group. When a tartrate ion binds at the aluminium, it binds first at the aluminium with one of the oxygen atoms from a carboxylate group. This is followed by another oxygen atom from the tartaric ion binding to
another aluminium atom. Duncan et al. [40] studied the adsorption of monotaartrate (C₄H₅O₆) and bitartrate (C₄H₄O₆) on the copper (110) surface and found the most probable way for a tartrate ion to get adsorbed at the surface is to bind with both the oxygen atoms from the carboxylate group (COO⁻) at two neighbouring top sites. In the case of a bitartrate ion it also binds with the other carboxylate group at the surface. The distance between the oxygen atoms from the carboxylate group that bind at the surface at Cu top positions is then 2.2 ± 0.1 Å. The distance between the oxygen atoms from the carboxylate group in the simulations is comparable, the distance between two aluminium top sites however, is larger. It can therefore be expected that the tartaric ion will bind to an aluminium surface in a different orientation than to a copper surface. In the simulation without an electric field being applied, a hydrogen atom from a hydroxyl group bonded to the second carbon atom, counting from left to right in Figure 6.4a, is seen to transfer to an oxygen atom bonded to the fourth carbon atom, Figure 6.4b. The tartaric ion then binds to the aluminium with one oxygen atom bonded to the first carbon atom and the oxygen atom bonded to the second carbon atom, Figure 6.4c. At the end of the simulation the tartaric ion is bonded to the surface with four oxygen atoms as can be seen in Figure 6.5. The hydrogen atom bonded to the oxygen atom of the fourth carbon atom has combined with the hydroxyl group of the third carbon atom to form a water molecule. The tartaric ion is bonded to the aluminium with oxygen atoms bonded to the first, second and fourth carbon atom.

![Image of tartaric ion binding at aluminium surface from simulation](a) (b) (c)

Figure 6.4: Tartaric ion binding at aluminium surface from simulation with an aluminium slab and ammonium tartrate dissolved in water at 300 K and without an electric field applied. Upon approaching the aluminium surface, Figure 6.4a, a hydrogen atom from the hydroxyl group of the second carbon atom, counting from left to right, is transferred to an oxygen atom bonded to the fourth carbon atom, Figure 6.4b. The tartaric ion then binds at the aluminium surface with two oxygen atoms bonded to the first and second carbon atom, Figure 6.4c. Blue spheres represent aluminium, red spheres represent oxygen, green spheres represent carbon and grey spheres represent hydrogen. For clarity only the tartaric ion and a part of the aluminium surface are shown. Although not visible in this representation the second carbon atom has also a hydrogen atom bonded to it and the oxygen atom bonded to the third carbon atom is part of a hydroxyl group.

**Structure of oxide layer**

The structure that results for the different field strengths, as shown in Figure 6.2, is a much more open structure than for oxidation in an atomic oxygen environment. Just as in the simulations with pure water, the oxide layer consists not only of aluminium and oxygen, there are hydroxyl groups, hydrogen atoms and water molecules in the layer as well. Chains of four carbon atoms, resulting from the tartaric ions, are also found in the oxide layer, with or without oxygen and hydrogen atoms still bonded to it.
Reactions

During the oxidation process the tartaric ions, either in the oxide layer or in the solution, are seen to lose the hydroxyl groups bonded to the middle carbon atoms. Some of these hydroxyl groups end up in the oxide layer as hydroxyl groups or have dissociated into oxygen and hydrogen. Other hydroxyl groups have bonded with a hydrogen atom to form a water molecule. These hydrogen atoms result from the dissociation of water in the formation of the oxide layer or from the ammonium ions that have dissociated into ammonia ($\text{NH}_3$) and hydrogen, according to

$$\text{NH}_4^+ \iff \text{NH}_3 + \text{H}^+. \quad (6.1)$$

In a solution where the concentration of hydrogen ions is low, the equilibrium for this reaction is expected to shift to the right. The hydroxyl groups in the solution will combine with a proton from the ammonium forming water and ammonia. In the simulations however, upon the formation of an oxide layer, the concentration of hydrogen ions, or hydronium ions, increases. The equilibrium for equation 6.1 is then expected to shift to the left, leaving more ammonium ions.

At the start of the simulation there was no true chemical equilibrium, since all ammonium tartrate molecules where placed in a dissociated state in the simulation box as tartrate ions and ammonium ions. The occurrence of the reaction described in equation 6.1 to form an equilibrium between ammonium and ammonia could therefore be expected. In the simulations however a higher concentration of hydrogen ions, resulting from more dissociation of water, occurring at a higher field strength, leads to the formation of more ammonia.

The $pK_a$ for reaction 6.1 equals 9.25 [38]. This value holds for a dilute aqueous solution at 298 K. In a real system there will be a large amount of water so that reactions close to the interface can be accommodated for by this large amount of water, leaving the overall equilibrium value unchanged. In the simulations however, the size of the system is too small to correctly capture the statistical averaged value for the dissociation constant.

6.2.2 Influence of native oxide layer on the anodizing of aluminium in an ammonium tartrate solution

For the simulations with aluminium covered with a native oxide layer and ammonium tartrate dissolved in water the resulting number of oxygen atoms in the oxide layer is shown in Figure 6.6.
Figure 6.6: Number of adsorbed oxygen atoms in oxide layer for simulations with aluminium covered with a native oxide layer and ammonium tartrate dissolved in water at 300 K and at different electric field strengths.

The adsorption of oxygen in the oxide layer as function of the electric field strength is comparable with the adsorption of oxygen in a pure water environment, Figure 4.14a. With a bare aluminium surface the tartaric ion assists in the formation of an oxide layer by adsorbing at the surface, which leads to charge transfer. As a result of this charge transfer, positively charged aluminium ions can move out of the surface layer, assisted by the electric field, and water molecules can dissociate at the surface. Starting with a native oxide layer the initially oxygen ended oxide layer changes, through ion movement enforced by the electric field, into an aluminium ended oxide layer. The tartaric ion binds to aluminium ions at the oxide surface. This results in charge transfer, making the aluminium ions binded to a tartaric ion more positively charged than those binded to only oxygen. This however does not result, as in the case of a bare aluminium surface, to more dissociation sites for water. The oxidation rate is therefore not increased by the presence of a tartaric ion.

From Figure 6.6 it becomes clear once more that the growth of the oxide layer in water or an electrolyte is determined by the dissociation of water. To study the anodization process in more detail it is therefore necessary that the dissociation of water is accurately described.

The results from the simulations performed in this chapter and those performed in the previous chapters are summarized in Table 6.1.
Table 6.1: Summary of results obtained in simulations. An empty field means there is no information available for that field. Details regarding the results can be found in chapters 3, 4, 5 and 6.

<table>
<thead>
<tr>
<th></th>
<th>Atomic oxygen</th>
<th>Water</th>
<th>Oxalic acid</th>
<th>Ammonium tartrate</th>
<th>Water + native oxide layer</th>
<th>Oxalic acid + native oxide layer</th>
<th>Ammonium tartrate + native oxide layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Described in chapter 3</td>
<td>Described in chapter 4</td>
<td>Described in chapter 5</td>
<td>Described in chapter 6</td>
<td>Described in chapter 4</td>
<td>Described in chapter 5</td>
<td>Described in chapter 6</td>
</tr>
</tbody>
</table>

### Influence of temperature
- Yes

### Influence of electric field
- Yes, for all field strengths
- Yes, only ≥ 1.5 V/Å
- Yes, only ≥ 1.7 V/Å
- Yes, only ≥ 1.0 V/Å
- Yes, dependent on structure of native oxide layer
- Yes, for all field strengths

### Rate determining step in oxidation process
- Ion movement
- Dissociation of water
- Dissociation of water
- Dissociation of water
- Dissociation of water
- Dissociation of water

### Critical electric field strength for ion movement
- Yes
- No
- No
- Yes
- No
- No
- No

### Dissociation of water
- ≥ 1.5 V/Å
- ≥ 1.7 V/Å
- ≥ 1.0 V/Å
- Yes
- Yes
- Yes

### Influence of vacancies
- No
- No
- Yes

### Influence of ions
- No
- No
- No
- Yes
- Yes
- Yes
Chapter 7

Discussion of methods

The simulations with a bare aluminium surface and water, section 4.2, show the formation of an oxide layer to start from an electric field strength of 1.5 V/Å on. At this field strength aluminium atoms from the surface plane are seen to move out of this surface plane, even without a water molecule dissociating next to them at the surface and creating charge transfer between the aluminium and the hydroxyl group. The field strength needed in these simulations to bring about dissociation of water seems to be too high regarding the behaviour of the aluminium. In simulations with water and a native oxide layer, section 4.2.4, although some dissociation of water molecules is seen, even for electric field strengths of 2.0 V/Å the growth of the oxide layer stops, since there is no new oxygen available for the formation of the oxide layer because no water molecules dissociate anymore towards the end of the simulation. In the simulations with a bare aluminium surface and an oxalic acid solution, section 5.2, or ammonium tartrate dissolved in water, section 6.2.1, the field strength needed to get dissociation of water molecules and with that the formation of an oxide layer equals 1.5 respectively 1.0 V/Å. With these solutions and aluminium covered with a native oxide layer, sections 5.2.3 and 6.2.2, the oxidation process stopped, just as with pure water, for all electric field strengths.

Saitta et al. [37] describe the field strength needed to have frequent dissociation of water molecules to be 0.35 V/Å. Since the anodization process is for a large part determined by the dissociation of water, it is necessary that this behaviour is accurately described. Although the methods used in this study to model the anodization process have a strong physical background, in order to describe the processes at an atomic scale with reasonable computational costs, assumptions had to be made, that can influence the accuracy of the results. The implementation of the electric field in the simulations, the procedure to calculate the charges and the parameterization of the force field all influence the obtained results and will therefore be elucidated in this chapter.

7.1 Contribution of electric field to energy

In the current implementation of ReaxFF in LAMMPS the contribution from the electric field on the energy is not taken into account. Since the charges are determined by minimizing the energy, taking the contribution from the electric field into account should modify the charge distribution and with that also the dissociation behaviour of water and the oxidation behaviour of aluminium in water. The same modification is made by Assowe et al. [18] for their study of nickel and water, and by Jeon et al. [19] in their study of the nanoscale oxidation of iron.

As explained in section 2.4 with equation 2.14, the force working on a charge $Q$ due to an external electric field is given by

$$\mathbf{F} = Q \mathbf{E}. \quad (7.1)$$

If this charge $Q$ would be displaced a small distance $\mathbf{ds}$, the work $dW$ needed to achieve this is [41]
\[ dW = -\mathbf{F} \cdot d\mathbf{s}. \]  
\[ (7.2) \]

Displacing the charge \( Q \) from its original position \( A \) to a position \( B \) and assuming the charge remains constant upon displacement, would acquire an amount of work

\[ W = \int_A^B dW = -\int_A^B Q\mathbf{E} \cdot d\mathbf{s}. \]  
\[ (7.3) \]

Since the electric field is related to the external potential as given by equation 2.13, it follows that

\[ W = Q \{ \phi(B) - \phi(A) \}. \]  
\[ (7.4) \]

The work needed to displace charge \( Q \) from point \( A \) to point \( B \) is equal to the change in potential energy if this is a reversible process. If there is no energy loss due to for instance radiation or collisions with other particles, the work is given by

\[ W = V_e(B) - V_e(A). \]  
\[ (7.5) \]

By comparing equation 7.4 and 7.5 it follows that

\[ V_e(B) = Q\phi(B) + \text{constant}. \]  
\[ (7.6) \]

By requiring that there is no interaction over an infinite distance, with other words, requiring that the potential energy is zero if the charge \( Q \) is positioned at an infinite distance from all other charges, the constant can be determined. If the point \( B \) goes to infinity, \( V_e(B) \) should be zero. To make the constant zero, \( \phi(B) \) should be zero at infinity and

\[ V_e(B) = Q\phi(B). \]  
\[ (7.7) \]

In the case of a homogeneous electric field, there is a charge distribution at infinity. The constant can therefore not be determined in this way. Only differences between potentials are than meaningful physical quantities.

The potential energy for a dipole and higher multipoles in an electric field is given by

\[ \begin{align*} 
n &= 0 \quad V_e &= Q\phi \\
n &= 1 \quad V_m &= \mathbf{m} \cdot \nabla \phi = -\mathbf{m} \cdot \mathbf{E} \\
n &= n \quad V_{n} &= \mathbf{Y}^{(n)} \cdot \nabla^n \phi(r), \end{align*} \]  
\[ (7.8) \]

where \( \cdot \) is used to denote a \( n \) times repeated inner multiplication and \( \nabla^n \) means a \( n \) times repeated product of \( \nabla \). In a homogeneous external field \( \nabla \mathbf{E} = 0 \) and the potential energy of a quadrupole and all higher multipoles is zero.

If not just a point charge, but a charge distribution of \( n \) charges \( Q_i \) in an external field is considered, the potential energy \( V \) is given by

\[ V = \sum_{i=1}^{n} Q_i \phi(r_i), \]  
\[ (7.9) \]

where \( \phi \) is the potential of the external field and \( r_i \) is the position of charge \( Q_i \).

In the current implementation of LAMMPS the potential energy from the external potential is not taken into account. Since in LAMMPS not the external potential is known, but the external electric field strength, the potential energy of the external potential should be written in terms of the external electric field strength, in order to modify the implementation and take this energy into account. Developing all potentials \( \phi(r_i) \) in a Taylor series around the origin leads to
\[ V = \sum_{i=1}^{n} Q_i \left[ \phi(0) + \mathbf{r}_i \cdot \nabla \phi(0) + \frac{1}{2} \mathbf{r}_i : \nabla \nabla \phi(0) + \ldots \right]. \]  

(7.10)

With the constraint that the total charge of the system is zero, the first term of equation 7.10 will become zero. In the case of a uniform field \( \nabla \phi(0) = -\mathbf{E} \) and \( \nabla \nabla \phi(0) = 0 \) which leads to the potential energy induced by the external potential,

\[ V = -\sum_{i=1}^{n} Q_i \mathbf{r}_i \mathbf{E}. \]  

(7.11)

If this potential energy is added to the electrostatic energy as given in equation 2.8, this results in

\[ E(Q_1, \ldots, Q_N) = \sum_{A} \left( E_{A_0} + \chi_0^A Q_A + \frac{1}{2} Q_A^2 J_{AA}^0 \right) + \sum_{A < B} Q_A Q_B J_{AB} - \sum_{A} Q_A r_A \mathbf{E}. \]  

(7.12)

The atomic-scale potential, equation 2.10, then becomes

\[ \chi_A(Q_1, \ldots, Q_N) = \frac{\partial E}{\partial Q_A} = \chi_0^A + J_{AA}^0 Q_A + \sum_{B \neq A} J_{AB} Q_B - r_A \mathbf{E} \]

\[ = \chi^*_A + J_{AA}^0 Q_A + \sum_{B \neq A} J_{AB} Q_B, \]  

(7.13)

where \( \chi^*_A = \chi_0^A - r_A \mathbf{E} \).

### 7.1.1 Implementation in LAMMPS

As explained in section 2.3 the atomic-scale potential \( \chi_A \) is set equal for each particle in the system and the total charge of the system is kept constant in order to determine the charge on each particle. It is expected that taking the potential energy induced by the external electric field into account will change the charge distribution in a system and with that the reactions that occur. Therefore, in the current work, the adjusted atomic-scale potential as given by equation 7.13 is implemented in LAMMPS.

**Single water molecule**

For a single water molecule in a \( 20 \times 20 \times 20 \) Å³ simulation box at 300 K and at different field strengths, the charges obtained with and without the modification of the energy to account for the energy of the electric field are shown in Figure 7.1a for different electric field strengths. Here it can be seen that applying an external electric field to a water molecule will lead to stronger polarization of this molecule, meaning there will be a more pronounced difference in the hydrogen and oxygen charges. In Figure 7.1b it can be seen that the oxygen-hydrogen bond length is hardly influenced by the electric field and by the modification of the energy.

The behaviour of a water molecule in an external electric field can be explained by considering the polarity of the molecule. Water is a polar molecule, which means that it has a permanent dipole \( \mu \). When an electric field is applied the positive and negative charges of this molecule move with respect to each other, leading to changes in the dipole and higher multipole moments. The total moment when a field is applied is defined \( \mathbf{m} \). The induced dipole \( \mathbf{p} \) is then given by

\[ \mathbf{p} = \mathbf{m} - \mu. \]  

(7.14)

This induced dipole is a function of the applied field strength \( \mathbf{E} \),

\[ \mathbf{p} = \alpha \mathbf{E}, \]  

(7.15)
where \( \alpha \) is the polarizability of the molecule.

The amount of work needed to place a neutral molecule with a permanent dipole \( \mu \) in an external field is given by [41]

\[
W = -\mu \cdot E - \frac{1}{2} \mathbf{E} \cdot \alpha \cdot \mathbf{E}.
\] (7.16)

The translational force working on this molecule is given by

\[
\mathbf{F} = -\nabla W = \mu \cdot \nabla \mathbf{E} + \mathbf{E} \cdot \alpha \cdot \nabla \mathbf{E},
\] (7.17)

which will be zero in a homogeneous field, since the gradient of the external field will be zero for a homogeneous field. This means that in a homogeneous field the molecule will not be translated. The molecule can rotate however, due to the torque working on it. This torque will tend to orient the dipole moment in the direction of the external field. The angle between the direction of the field and the dipole moment vector is \( \theta \). The torque is given by

\[
T_\theta = -\frac{\partial W}{\partial \theta}.
\] (7.18)

In both simulations, with and without the modification of the energy to account for the energy of the external electric field, the water molecule was oriented in the direction of the field, but was not translated as follows from equations 7.17 and 7.18.

### Multiple water molecules

For a larger system, containing more water molecules, a computational problem arises. If an atom crosses the boundary of a simulation box, it will enter the box at the opposite side due to the periodic boundary conditions applied. A molecule consisting of more than one atom can therefore be partly at one and partly at the other side of a simulation box. The potential energy due to the electric field, equation 7.11, and with that the atomic-scale potential as given in equation 7.13, has now become dependent on the position of the atom. For atoms crossing a periodic boundary in the direction in which the electric field works, this leads to a discontinuity in the external potential felt by that atom and therefore to unphysical results. In the direction in which there exists an external potential there can be no periodic boundary condition applied if atoms are allowed to cross this boundary or have an interaction with atoms at the other side of this boundary.
To compare the charges calculated on the oxygen and hydrogen ions from water molecules for a larger system, a system is modelled consisting of 212 water molecules. The simulation box measures $20 \times 20 \times 20 \, \text{Å}^3$, is centered around the origin and has periodic boundary conditions in the x- and y-direction. The z-direction is bounded by reflecting walls to prevent atoms from leaving the simulation box. An electric field of 1.0 V/Å is placed over the simulation box in the positive z-direction. Simulations are performed with and without the modification of the energy as described above. These simulations are performed with a constant volume at 300 K with a time step of 0.1 fs and lasted 1 ps. The resulting charges of the oxygen and hydrogen atoms are shown in Figure 7.2.

![Figure 7.2](image)

(a) Original implementation of electric field in LAMMPS.

(b) Adjusted implementation to take energy of electric field into account.

Figure 7.2: Charges on oxygen and hydrogen atoms for 212 water molecules in a $20 \times 20 \times 20 \, \text{Å}^3$ sized simulation box, centered around the origin, with periodic boundary conditions in the x- and y-direction and an electric field of 1.0 V/Å working in the z-direction. The simulations were performed at 300 K with constant volume and lasted 1 ps with a time step of 0.1 fs.

From this figure it becomes clear that with and without the modification of the energy to account for the energy of the electric field, there are boundary effects. The charges of the atoms at the edges of the simulation box are different than those of atoms in the bulk. This can be explained by the different environment for molecules at the edges with respect to molecules in the bulk. The water molecules, on top of the external electric field, feel an electric field induced by the water molecules surrounding them. This field will clearly be different for molecules in the bulk than for molecules at the edges.

The most important conclusion that can be drawn from Figure 7.2 is that the modification of the energy to account for the energy of the external electric field, makes the charge of an atom dependent on the position of that atom. For a system containing neutral water molecules equations 7.17 and 7.18 show that a homogeneous external electric field will only lead to the rotation of these molecules and not to displacement of these molecules. The expected effect of an external electric field on the charge distribution in the molecules is a more pronounced charge difference within a molecule, preserving the neutrality of the molecule. What is seen in the simulations however, is a charge distribution in the system with the charge of the molecule dependent on the z-position of the molecule. A lower z-position gives a lower charge while a higher z-position gives a higher charge.

In equation 7.10 to determine the potential energy contribution of the external potential $\phi$, all potentials $\phi(r_i)$ where developed in a Taylor series around the origin. The choice of this origin will not influence the potential energy contribution of the external potential, since this is invariant to translations. If the whole system would be translated according to the vector $\mathbf{c}$, the new atom
positions would become \( r_i + c \). The energy contribution from the external potential would equal

\[
V = - \sum_{i=1}^{n} Q_i (r_i + c) E
= - \sum_{i=1}^{n} Q_i r_i E - \sum_{i=1}^{n} Q_i c E.
\] (7.19)

The last summation in equation 7.19 equals zero, since the sum over all charges was set to zero, equation 2.12. Equation 7.19 therefore becomes equal to equation 7.11 and the energy contribution of the external potential is shown to be invariant to translations of the system.

The charge distribution in all simulations, as explained in section 2.3, is determined with a charge equilibration procedure QEq. The awkward charge distribution resulting when the energy of the external potential is taken into account, is a result of this QEq-procedure as will be explained in the next section. Given the charge distribution that results if the energy of the external potential is taken into account, it is not possible in the present study of the anodization of aluminium to use this modification of the energy. The awkward charge distribution as calculated for an aluminium slab and water as shown in Figure 4.5b, where positively and negatively charged aluminium planes are seen, becomes more pronounced if the energy of the external potential is taken into account. The aluminium slab shows charged planes, where the charges become more pronounced than without the modification of the energy. Just as shown in Figure 7.2 on average a higher z-position leads to a higher charge. This leads to unphysical reactions and therefore all simulations regarding the anodization of aluminium are performed without taking the energy of the external electric field into account.

### 7.2 Charge distribution calculated by QEq-procedure

The remarkable observation made in section 4.2 that the charge distribution calculated by ReaxFF is such that on average the aluminium is positively charged, while the water is negatively charged, can be explained if the QEq procedure is analyzed. According to equation 2.10 the atomic-scale potentials for two atoms \( A \) and \( B \) with charges \( Q_A \) and \( Q_B \) in a vacuum are given by

\[
\chi_A = \chi_0^A + J_{AA}^0 Q_A + J_{AB} Q_B
\]
\[
\chi_B = \chi_0^B + J_{BB}^0 Q_B + J_{BA} Q_A.
\] (7.20)

If these two atoms are infinitely far apart, there will be no Coulomb interaction between them and both \( J_{AB} \) and \( J_{BA} \) will be zero. In the QEq-procedure, for the system to be in equilibrium, the total charge of the system is set to zero and the electrostatic energy is minimized by setting the atomic-scale potentials for atom \( A \) and \( B \) equal, equation 2.11 and 2.12. This results in

\[
\chi_A^0 + J_{AA}^0 Q_A = \chi_B^0 + J_{BB}^0 Q_B.
\] (7.21)

Since \( Q_A + Q_B = 0 \), \( Q_A = -Q_B = Q \) and

\[
Q = \frac{\chi_B^0 - \chi_A^0}{J_{AA}^0 + J_{BB}^0}.
\] (7.22)

For two identical atoms, this means both atoms have a charge equal to zero since they both have the same electronegativity \( \chi^0 \). For two atoms of a different species however, both atoms will have a charge not equal to zero. They will have a charge opposite in sign depending on their electronegativity and Self-Coulomb potential. However, in reality two atoms in vacuum at an infinite distance from each other have no possibility for charge transfer and should therefore both have a charge equal to zero.
The QEq procedure is based on the electronegativity equalization method (EEM) by Mortier et al. [42]. This method originally was derived for a single molecule. To determine the charge distribution in a molecule, it is assumed that the charges are distributed in such a way that the electronegativity is equal for each atom in that molecule. If this was not the case, the electron density from the atoms would shift from atoms with higher to atoms with lower electronegativity. This would make the electronegativity equal everywhere in the molecule. The equilibrium charge distribution for a molecule with specified atom positions is therefore that particular charge distribution in which the electronegativity is equal everywhere in the molecule.

In order to achieve this electronegativity equalization in EEM the derivative of the electrostatic energy with respect to the charge, which is the electronegativity, is set equal for each atom of that molecule under the constraint that the total charge of the molecule remains unchanged. For a system containing only one molecule, this should lead to a meaningful distribution of charges. Although the original EEM method was developed to describe only one molecule, the model has been used extensively to describe systems consisting of more than one molecule. For a conducting system like a metal, the charges can still be expected to be properly described. For other systems consisting of multiple molecules the assumption that the electronegativity is equal will hold within each molecule, but does not have to hold for different molecules. This is however how it is currently implemented in the QEq procedure in ReaxFF.

To model the anodization process as described in the previous chapters, the long-range charge transfer allowed by QEq gives awkward results. In a theoretic view of an aluminium slab in contact with water, the aluminium slab and the water molecules would be neutral, with only some interaction, charge transfer, at the interface. Without an electric field, the surface layer of the aluminium would become positively charged, while the adsorbed water layer gets a negative charge. Upon applying an electric field, the neutral bulk aluminium would not feel a force from this field. The water molecules in the water bulk, would feel this field and align their dipoles in the direction of the field. They would not get displaced, since every molecule is neutral. The aluminium atoms and water molecules at the interface are charged and will therefore be influenced by the electric field.

In the current situation however, the water molecules above the adsorbed surface layer are not neutral, Figure 4.5b. On average these water molecules are negatively charged. Applying an electric field over the whole simulation box will place a downwards force on the negatively charged water molecules, making them move towards the aluminium slab. The aluminium slab in the simulations has as expected a positively charged surface layer. The second aluminium layer however is negatively charged, with a more negative charge than the adsorbed water layer. The third and fourth aluminium layer have a small positive charge. The force from the electric field will push the surface layer upwards, while the second layer is pulled down.

As described in section 4.1 the electric field in the simulations is placed only over the oxide layer to prevent unwanted effects. The charge distribution calculated by QEq influences, as is shown in section 4.2.1, the reactions that take place.

If an external electric field is applied in the simulations, the contribution of this electric field to the energy of the system should be taken into account, as explained in section 7.1. Here it was also shown that for a system containing more than one molecule, this leads to unphysical results. These results can be explained by the unphysical probability for long-range charge transfer given by the QEq-procedure. For all atoms in the system the atomic-scale potential, if the energy contribution from the external electric field is taken into account, is given by equation 7.13. For the system containing 212 water molecules described in the previous section, it can be seen that in order to make all atomic-scale positions equal, atoms at a higher z-position $r_A$ should have a higher charge $Q_A$ and vice versa, atoms at a lower z-position should have a lower charge. This is exactly what is seen in Figure 7.2b.

For a non-conducting system consisting of more than one molecule the electronegativity equalization should be performed locally, that is, within each molecule. The constraint on the charge
to remain unchanged for the total system naturally should still hold. The total charge of individual molecules should also be constrained, however, upon breaking or formation of molecules, the charge should from that moment on be constrained for the resulting fragments or molecules. This constrained charge, especially for ionic fragments, should not be necessarily constrained at zero. If a molecule, for which the total charge is constrained, dissociates into two ionic fragments, from that moment on for each fragment the total charge should be constrained. And vice versa, if two ionic fragments combine to form a molecule, from that moment on the charge, not of the individual fragments, but of the total molecule, should be constrained.

The breaking and formation of bonds, as described by ReaxFF, is not a discrete process. All atoms vibrate and therefore the distance between atom pairs is constantly changing. The bond order is determined based on the bond length. Due to the constantly changing bond length an atom can be bonded to another atom at a certain time step, while it is considered to be non bonded the next time step, and bonded again afterwards. Changing the constraint from molecule to fragment back to molecule will computationally be very challenging.

Since the first publication of Mortier et al. [42] in which they propose their electronegativity equalization method EEM in 1986 several approaches have been made to improve the EEM procedure and describe the charge distribution and with that the formation and dissociation of molecules more accurately.

Nistor et al. [43], proposed split charge equilibration (SQE). The charge of each atom is split in contributions of charge flow between the atom and all of its covalently bonded neighbours,

$$Q_i = \sum_j \bar{q}_{ij}. \quad (7.23)$$

This method, like EEM, is based on charge equilibration, but charges are only allowed to flow between covalently bonded neighbours.

Mikulski et al. [44] merged the split charge equilibration with a bond order potential into BOP/SQE. The asymmetry of the charge sharing in a bond is determined by the equilibration procedure, while the quantity of charge to be shared is determined by the bond order.

If charges are split only for covalently bonded atom pairs (SQE) or the amount of charge to be shared between atom pairs goes to zero for a bond-order zero (BOP/SQE), there can be no intermolecular charge transfer and only neutral molecules can be described.

Chen and Martínez [45] proposed the QTPIE method for charge transfer with polarization current equilibration. This model is not based on atomic partial charges but on charge transfer variables that describe a polarization current. In contrast to EEM the charges on the two atomic fragments of a diatomic molecule approach zero when the distance between the fragments approaches infinity. Later [46] this model was reformulated in terms of atomic charge variables to reduce computational costs.

Müser [47] and Verstraelen et al. [48] extended the SQE method to describe charged molecules. This solution is based on empirical grounds and has no profound theoretical basis.

Verstraelen et al. [49] proposed the atom-condensed Kohn-Sham DFT approximated to second order (ACKS2) to correctly describe atomic charges when covalent bonds break or form. This method is not yet capable to describe non neutral molecules.

To properly model the anodization of aluminium the charge equilibration procedure should be adjusted based on the considerations described above.

7.3 Comparison of ReaxFF with RFMEAM + CTIP potential

To determine how accurate the ReaxFF implementation for aluminium, hydrogen and oxygen [27] predicts the minimum energy, lattice constant and charges for different crystal structures of aluminium and oxygen, these are calculated and compared with those obtained with the RFMEAM + CTIP potential for aluminium and oxygen by Lazić and Thijsse [50, 51].
Table 7.1: Minimum energies and lattice constants for different Al$_x$O$_y$ crystals for \textit{ab initio} calculations and the RFMEAM + CTIP potential [51] and the ReaxFF potential for aluminium, hydrogen and oxygen.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>\textit{ab initio} calculations</th>
<th>RFMEAM + CTIP</th>
<th>ReaxFF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum energy (eV)</td>
<td>Lattice constant (Å)</td>
<td>Minimum energy (eV)</td>
</tr>
<tr>
<td>1 AlO (NaCl)</td>
<td>-4.55</td>
<td>4.33</td>
<td>-4.63</td>
</tr>
<tr>
<td>2 AlO (CsCl)</td>
<td>-4.05</td>
<td>2.68</td>
<td>-4.50</td>
</tr>
<tr>
<td>3 AlO (CuAu)</td>
<td>-3.54</td>
<td>3.44</td>
<td>-3.02</td>
</tr>
<tr>
<td>4 AlO (ZnS)</td>
<td>-5.12</td>
<td>4.41</td>
<td>-6.53</td>
</tr>
<tr>
<td>5 Al$_2$O (Co$_2$B)</td>
<td>-3.79</td>
<td>5.49</td>
<td>-3.81</td>
</tr>
<tr>
<td>6 Al$_3$O (Fe$_4$C)</td>
<td>-3.99</td>
<td>4.18</td>
<td>-4.05</td>
</tr>
<tr>
<td>8 Al$_3$O (Ni$_3$P)</td>
<td>-3.65</td>
<td>9.47</td>
<td>-3.96</td>
</tr>
<tr>
<td>9 AlO$_2$ (CaF$_2$)</td>
<td>-5.38</td>
<td>4.67</td>
<td>-5.36</td>
</tr>
<tr>
<td>10 O in FCC Al, Al$_{32}$O</td>
<td>-3.58</td>
<td>4.05</td>
<td>-3.57</td>
</tr>
<tr>
<td>11 Al$<em>{20}$O$</em>{16}$</td>
<td>-3.75</td>
<td>6.79</td>
<td>-3.94</td>
</tr>
<tr>
<td>12 $\alpha$-Al$_2$O$_3$</td>
<td>-6.60</td>
<td>4.76</td>
<td>-6.60</td>
</tr>
<tr>
<td>13 $\gamma$-Al$_2$O$_3$ - Fd3m</td>
<td>-6.53</td>
<td>7.91</td>
<td>-5.14</td>
</tr>
</tbody>
</table>

The energy of a system of N atoms consists of the electrostatic energy $E_{es}$ and the non-electrostatic energy $E_{nes}$,

$$E = E_{es} + E_{nes}. \quad (7.24)$$

In the RFMEAM + CTIP potential the electrostatic part, CTIP, is fitted first and then the non-electrostatic part, RFMEAM, is fitted making use of the data obtained by CTIP. The combination of these two gives the full potential. This potential has shown to correctly predict $\alpha$-Al$_2$O$_3$ to be the most stable structure. The atomic charges, lattice constants and crystal energies predicted by this potential are more realistic than other potentials have shown.

In Table 7.1 the minimum energies and the corresponding lattice constants for different Al$_x$O$_y$ crystals are given as calculated with \textit{ab initio} calculations [51], the RFMEAM + CTIP potential [51] and with the ReaxFF potential for aluminium, hydrogen and oxygen.

In Figure 7.3 the minimum energies for the different crystals as calculated by RFMEAM + CTIP and ReaxFF are compared with those calculated with \textit{ab initio} calculations. Here it can be seen that both \textit{ab initio} calculations and the RFMEAM + CTIP potential predict $\alpha$-Al$_2$O$_3$ to be the most stable structure. ReaxFF however calculates a lower energy for AlO with a ZnS structure.

The charges on the oxygen and aluminium atoms in the various crystal structures as calculated by RFMEAM + CTIP and ReaxFF are given in Table 7.2 and compared in Figure 7.4. From this figure it can be seen that the charges calculated by ReaxFF are always less than those calculated by RFMEAM + CTIP.

Although the RFMEAM + CTIP potential seems to give more realistic results regarding minimum energies and charges than ReaxFF, this does not mean that this potential is more appropriate to use in the current simulations. There are several issues preventing simulations regarding the anodization of aluminium to be performed with RFMEAM + CTIP. The first problem that arises is that the RFMEAM + CTIP potential has been only fitted for aluminium and oxygen. To run simulations including water or acids, it would have to be fitted to include hydrogen, carbon and nitrogen.

Second, camelion, the molecular dynamics program for which the RFMEAM + CTIP potential is currently written, can only run on a single processor. LAMMPS, an acronym for Large-scale
Minimum energies (eV), ab initio calculations

RFMEAM + CTIP
ReaxFF

Figure 7.3: Minimum energies calculated with RFMEAM + CTIP [51] and ReaxFF compared with the minimum energy calculated with ab initio calculations [51]. The black lines are drawn as a guide for the eye. The diagonal line represents the minimum energy calculated by ab initio calculations. The vertical dashed lines represent one specific crystal structure.

Atomic/Molecular Massively Parallel Simulator, as the name already indicates is developed to run in parallel. This results in large time savings compared with running on a single processor.

The third problem that arises is that in order to study the anodization of aluminium an electric field must be applied in the simulations. In camelion it is not yet possible to apply an electric field in a simulation.

The electron density distribution around an atom is assumed to be a spherically symmetric Gaussian distribution in RFMEAM + CTIP. Polarization effects, which would result from an electric field, can therefore not be taken into account. In the QEq-procedure used in ReaxFF spherically symmetric Slater-type atomic orbitals are assumed while in EEM spherically symmetric Gaussian-type atomic orbitals are assumed to determine the Coulomb interaction between two atom centers. Electronic polarization can therefore not be correctly described by QEq and EEM as well.

The above described limitations of the RFMEAM + CTIP potential can be solved with more or less ease. The major problem that has raised in the simulations performed with ReaxFF are a result from the charge equilibration procedure. In the CTIP procedure the total electrostatic energy is minimized with the constraint that the total charge of the system is zero. Just as in the QEq procedure the derivatives of the electrostatic energy with respect to the charge are set equal for each charge. The problems arising from the QEq procedure used in ReaxFF, all related to the possibility of long-range charge transfer even through vacuum, can be expected to arise in
Table 7.2: Charges on oxygen and aluminium for different Al\textsubscript{x}O\textsubscript{y} crystals calculated with RFMEAM + CITP [51] and the ReaxFF parameterization for aluminium, hydrogen and oxygen.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>RFMEAM + CTIP</th>
<th>ReaxFF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q\textsubscript{Al} (e)</td>
<td>q\textsubscript{O} (e)</td>
</tr>
<tr>
<td>1 AlO (NaCl)</td>
<td>2.05</td>
<td>-2.05</td>
</tr>
<tr>
<td>2 AlO (CsCl)</td>
<td>2.04</td>
<td>-2.04</td>
</tr>
<tr>
<td>3 AlO (CuAu)</td>
<td>1.30</td>
<td>-1.30</td>
</tr>
<tr>
<td>4 AlO (ZnS)</td>
<td>2.09</td>
<td>-2.09</td>
</tr>
<tr>
<td>5 Al\textsubscript{2}O (Co\textsubscript{2}B)</td>
<td>1.02</td>
<td>-2.04</td>
</tr>
<tr>
<td>6 Al\textsubscript{3}O (Fe\textsubscript{4}C)</td>
<td>0.53</td>
<td>-2.10</td>
</tr>
<tr>
<td>8 Al\textsubscript{3}O (Ni\textsubscript{3}P)</td>
<td>0.68</td>
<td>-2.05</td>
</tr>
<tr>
<td>9 AlO\textsubscript{2} (CaF\textsubscript{2})</td>
<td>2.02</td>
<td>-1.01</td>
</tr>
<tr>
<td>10 O in FCC Al, Al\textsubscript{3}O</td>
<td>0.06</td>
<td>-2.03</td>
</tr>
<tr>
<td>11 Al\textsubscript{20}O\textsubscript{16}</td>
<td>1.62</td>
<td>-2.02</td>
</tr>
<tr>
<td>12 \textalpha-Al\textsubscript{2}O\textsubscript{3}</td>
<td>2.91</td>
<td>-1.94</td>
</tr>
<tr>
<td>13 \textgamma-Al\textsubscript{2}O\textsubscript{3} - Fd3m</td>
<td>2.18</td>
<td>-1.46</td>
</tr>
</tbody>
</table>

all potentials which use a charge equilibration procedure like QEq or EEM. These same problems are therefore likely to arise with the RFMEAM + CTIP potential.
Figure 7.4: Charges on aluminium and oxygen ions for different Al$_x$O$_y$ crystal structures as calculated with RFMEAM + CTIP [51] and the ReaxFF parameterization for aluminium, hydrogen and oxygen.
Simulations of the oxidation of aluminium in an atomic oxygen environment under the influence of an electric field show three different regimes in the oxidation process. For low field strengths, increasing the field strength increases only the initial adsorption rate of oxygen at the aluminium surface. Increasing the temperature has the same effect. The ion movement in the oxide layer in the remaining part of the simulation is not influenced by the field strength if this stays underneath a certain critical value. Above this critical field strength, which is lower for higher temperature, the ion movement is influenced and the adsorption rate during the whole simulation is increased. Increasing the field strength even further again influences the initial adsorption rate, while the adsorption rate after the first 100 ps is not influenced, until a second critical field strength is reached. Then the ion movement, and with that the adsorption rate, in the whole simulation is dramatically increased. The apparent existence of these critical field strengths can be explained by the energy barrier the ions have to overcome to migrate through the oxide layer. Only a high enough force makes it possible for the ions to overcome this energy barrier and migrate through the oxide layer, forming new aluminium oxide and creating new available surface sites for oxygen adsorption and thus increasing the adsorption rate.

The ion movement in the oxide layer does not consist of either aluminium or oxygen ions moving all the way through the oxide layer to react at the other interface. Instead the displacement of one ion causes the displacement of an other ion and so forth, until an aluminium ion is pushed out of the surface layer to react with oxygen at the oxide/gas interface or an oxygen ion reaches the aluminium/oxide interface and reacts with the aluminium.

The start of the oxidation of aluminium under the influence of an external electric field in the presence of pure water, is determined by the dissociation of water molecules. Only a high enough field strength leads to dissociation. Disrupting a perfect aluminium surface plane by creating a vacancy or starting with ions in the water that bind at the surface, does not significantly decrease the barrier for dissociation of water. The formation of an adsorbed water layer apparently is energetically more favourable. If the applied electric field is strong enough to enable dissociation of water molecules, an oxide layer grows that consists of water molecules, hydrogen atoms and hydroxyl groups, in addition to aluminium and oxygen ions.

With pure water the electric field strength needed for dissociation of water molecules seems to be too high to preserve realistic aluminium behaviour. At these high field strengths, aluminium is seen to move out of the surface plane, assisted by the electric field, without the presence of an adsorbed hydroxyl group next to it. In the presence of a tartaric acid solution however, the dissociation of water is facilitated by the adsorption of tartaric ions at the aluminium surface and takes place at a lower, and therefore more realistic, field strength then in a pure water environment. In this case the same regimes are seen in the oxidation process with respect to field strength as when oxidation proceeds in an atomic oxygen environment.

The behaviour of oxalic acid is not well described by the current parameterization of ReaxFF for aluminium, oxygen, carbon, hydrogen and nitrogen. Oxalic acid molecules become negatively
charged and attract hydrogen instead of dissociating. Refitting this ReaxFF parameterization to better describe the structures needed to model the anodization process, is necessary to improve the results of simulations involving oxalic and tartaric acids.

For an aluminium slab covered with a native oxide layer the dissociation of water is the rate determining step in the growth of the oxide layer. Applying an electric field over the oxide layer leads initially to rearrangements in the oxide layer. For all environments, being water, oxalic acid dissolved in water and ammonium tartrate dissolved in water, and for all field strengths at the end of the simulations there is hardly any dissociation of water molecules seen. Without the presence of new oxygen atoms formed upon dissociation of water there is no longer a driving force for ion movement in the oxide layer and the adsorption rate of oxygen in the oxide layer becomes zero.

Comparison of the ReaxFF parameterization for aluminium, hydrogen and oxygen with the RFMEAM + CTIP potential for several aluminium oxide crystal structures, shows the latter to describe more accurately the minimum energies and charges for most of these crystals. To actually use this potential to study the anodization of aluminium, it should be parameterized for more elements, including at least hydrogen and carbon.

In the standard implementation of an external electric field in LAMMPS the contribution from this electric field on the energy of the system, and with that on the charge distribution throughout the system, is not taken into account. In the current work the implementation was adjusted so that this contribution to the energy is accounted for. For one single molecule in an homogeneous external electric field this implementation gives reasonable results. However, taking the energy contribution from the external electric field into account for a system containing more than one molecule results in position dependent charges, due to the QEq-procedure applied for determining the charge distribution. In the simulations of the anodization of aluminium it was therefore not possible to take the energy contribution from the external electric field into account.

The charges predicted by ReaxFF influence the oxidation behaviour. In simulations with aluminium and oxygen a higher field strength is needed to compensate for the lower charges calculated by ReaxFF than would be expected based on other studies. When simulations are performed with aluminium and water or an aqueous solution, the charge distribution in the top layers of the aluminium slab is not realistic. A positively charged top layer results, followed by a negatively charged second layer and positively charged third and fourth layers. This charge distribution results in the aluminium becoming more dense under influence of the electric field. The dissociation of water molecules at the aluminium surface is negatively influenced by this charge distribution.

The charge distribution calculated by ReaxFF results from the QEq-procedure used for calculating the charges. The underlying assumption in this procedure, namely an equal value for the electronegativity for each particle in the system, is, although correct for single molecules or conducting systems, incorrect for the systems consisting of aluminium and water or an aqueous solution. In order to correctly describe the reactions between water, acids and aluminium, the QEq-procedure should be adjusted to avoid unrealistic long-range charge transfer.
Appendix A

Reax force field for aluminium, oxygen and hydrogen

Reactive MD-force field: Al force field/H2O force field Russo et al. IJHE 2011

39 ! Number of general parameters
50.0000 ! Overcoordination parameter
9.5469 ! Overcoordination parameter
26.5405 ! Valency angle conjugation parameter
1.7224 ! Triple bond stabilisation parameter
6.8702 ! Triple bond stabilisation parameter
60.4850 ! C2-correction
1.0588 ! Undercoordination parameter
4.6000 ! Triple bond stabilisation parameter
12.1176 ! Undercoordination parameter
13.3056 ! Undercoordination parameter
-70.5044 ! Triple bond stabilization energy
0.0000 ! Lower Taper-radius
10.0000 ! Upper Taper-radius
2.8793 ! Not used
33.8667 ! Valency undercoordination
6.0891 ! Valency angle/lone pair parameter
1.0563 ! Valency angle
2.0384 ! Valency angle parameter
6.1431 ! Not used
6.9290 ! Double bond/angle parameter
0.3989 ! Double bond/angle parameter: overcoord
3.9954 ! Double bond/angle parameter: overcoord
-2.4837 ! Not used
5.7796 ! Torsion/B0 parameter
10.0000 ! Torsion overcoordination
1.9487 ! Torsion overcoordination
-1.2327 ! Conjugation 0 (not used)
2.1645 ! Conjugation
1.5591 ! vdWals shielding
0.1000 ! Cutoff for bond order (*100)
2.1365 ! Valency angle conjugation parameter
0.6991 ! Overcoordination parameter
50.0000 ! Overcoordination parameter
1.8512 ! Valency/lone pair parameter
0.5000 ! Not used
20.0000 ! Not used
5.0000 ! Molecular energy (not used)
0.0000 ! Molecular energy (not used)
2.6962 ! Valency angle conjugation parameter
3 ! Nr of atoms; cov.r; valency; a.m; Rvdw; Evdw; gammaEEM; cov.r2;# alfa; gammavdW; valency; Eunder; Eover; chiEEM; etaEEM; n.u.
cov r3; Elp; Heat inc.; n.u.; n.u.; n.u.; n.u.
Appendix B

Reax force field for aluminium, oxygen, hydrogen, carbon and nitrogen

 Reactive MD-force field: Alumina/Epoxy(N-Al), Valega and Thijsse 2012

39: Number of general parameters

50.0000 ! Overcoordination parameter
9.5469 ! Overcoordination parameter
26.5405 ! Valency angle conjugation parameter
1.7224 ! Triple bond stabilisation parameter
6.8702 ! Triple bond stabilisation parameter
60.4850 ! C2-correction
1.0588 ! Undercoordination parameter
4.6000 ! Triple bond stabilisation parameter
12.1176 ! Undercoordination parameter
13.3056 ! Undercoordination parameter
-70.5044 ! Triple bond stabilization energy
0.0000 ! Lower Taper-radius
10.0000 ! Upper Taper-radius
2.8793 ! Not used
33.8667 ! Valency undercoordination
6.0891 ! Valency angle/lone pair parameter
1.0563 ! Valency angle
2.0384 ! Valency angle parameter
6.1431 ! Not used
6.9290 ! Double bond/angle parameter
0.3989 ! Double bond/angle parameter: overcoord
3.9954 ! Double bond/angle parameter: overcoord
-2.4837 ! Not used
5.7796 ! Torsion/B0 parameter
10.0000 ! Torsion overcoordination
1.9487 ! Torsion overcoordination
-1.2327 ! Conjugation 0 (not used)
2.1645 ! Conjugation
1.5591 ! vdWaals shielding
0.1000 ! Cutoff for bond order (*100)
2.1365 ! Valency angle conjugation parameter
0.6991 ! Overcoordination parameter
50.0000 ! Overcoordination parameter
1.8512 ! Valency/lone pair parameter
0.5000 ! Not used
20.0000 ! Not used
5.0000 ! Molecular energy (not used)
0.0000 ! Molecular energy (not used)
2.6962 ! Valency angle conjugation parameter
<p>| 1 | 1.582004 | 99.1897 | 78.0000 | -0.7738 | -0.4550 | 1.0000 | 37.6117 | 0.4147 |
| 2 | 1.694760 | 0.0000 | 0.0000 | -0.6083 | 0.0000 | 1.0000 | 6.0000 | 0.7652 |
| 3 | 100.9167 | 136.3836 | 65.3877 | 0.3895 | -0.396 | 1.0000 | 18.8159 | 0.6674 |
| 4 | 165.1874 | 148.6965 | 72.7249 | -1.3237 | -0.3504 | 1.0000 | 27.5446 | 0.1473 |
| 5 | 130.8596 | 169.4551 | 40.0000 | 0.3837 | -0.1639 | 1.0000 | 35.0000 | 0.2000 |
| 6 | 157.9384 | 82.5526 | 152.5336 | 0.4010 | -0.1034 | 1.0000 | 12.4261 | 0.5828 |
| 7 | 208.1369 | 0.0000 | 0.0000 | -0.3949 | 0.0000 | 1.0000 | 6.0000 | 0.3340 |
| 8 | 153.3934 | 0.0000 | 0.0000 | -0.4600 | 0.0000 | 1.0000 | 6.0000 | 0.7300 |
| 9 | 160.0000 | 0.0000 | 0.0000 | -0.5725 | 0.0000 | 1.0000 | 6.0000 | 0.5626 |
| 10 | 142.2858 | 145.0000 | 50.8293 | 0.2506 | -0.1000 | 1.0000 | 29.7503 | 0.6051 |
| 11 | 0.3451 | -0.1055 | 9.0000 | 1.0000 | -0.1225 | 5.5000 | 1.0000 | 0.0000 |
| 12 | 10.0000 | -0.3500 | 25.0000 | 1.0000 | -0.1000 | 8.0000 | 0.0000 | 0.0000 |
| 13 | 107.4452 | 0.0000 | 0.0000 | -0.6698 | -0.3000 | 0.0000 | 36.0000 | 0.1543 |
| 14 | 9.6122 | -0.3500 | 25.0000 | 1.0000 | -0.0867 | 7.1984 | 0.0000 | 0.0000 |
| 15 | 200.0000 | 0.0000 | 0.0000 | -1.0000 | -0.3000 | 0.0000 | 36.0000 | 0.0567 |
| 16 | 6.6332 | -0.3500 | 25.0000 | 1.0000 | -0.0740 | 5.4697 | 0.0000 | 0.0000 |
| 17 | 236.0719 | 0.0000 | 0.0000 | -1.5976 | -0.3000 | 0.0000 | 36.0000 | -0.0005 |
| 18 | 4.4084 | -0.3500 | 25.0000 | 1.0000 | -0.1268 | 4.0887 | 0.0000 | 0.0000 |
| 19 | 34.0777 | 0.0000 | 0.0000 | 0.4832 | -0.3000 | 0.0000 | 16.0000 | 0.5154 |
| 20 | 6.4631 | -0.4197 | 14.3085 | 1.0000 | -0.1463 | 6.1680 | 0.0000 | 0.0000 |</p>
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Bibliography


