Simulation of plasma-chemical kinetics of microdischarges formed in bubbles during plasma electrolytic oxidation

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Abstract: Plasma electrolytic oxidation (PEO) is characterised by complex and transient microdischarges occurring within gas bubbles on an electrode surface in a liquid electrolyte. This work aims to understand the plasma-chemical processes occurring in these systems using 0-D-plasma-chemical kinetics simulations informed by experimental measurements. The simulations reveal the complex chemical environment of these microdischarges and provide estimates of the concentrations of highly reactive species.

Keywords: Plasma electrolytic oxidation, plasma-liquid interactions, microdischarges

1. Introduction

Plasma-liquid interactions play an important role in many applications and are a subject of increasing interest. One such application is plasma electrolytic oxidation (PEO). PEO is a process based on anodic oxidation in liquid electrolyte solutions but compared to conventional anodisation, operates above the breakdown voltage. This results in dynamic and transient microdischarges contained in water-vapour bubbles that are used to create a passivation layer on light metals like aluminium, titanium, and magnesium, as well as on their alloys. The coating properties generally depend on the chosen electrolyte composition and the electrical parameters. [1]

Due to the complex nature of microdischarge formation and sustainment, there is still a relatively limited understanding of many fundamental properties in these systems, such as the concentration of reactive species produced. As a result, the potential role of these species on the overall process is not known. Such information is difficult to obtain from purely experimental studies as many diagnostic methods are either not possible at all or only with substantial difficulties due to the transient and stochastic nature of microdischarge formation. A fully self-consistent simulation of bubble and microdischarge formation and the associated plasma-chemical kinetics is also a substantial challenge.

This work focuses on understanding the plasma-chemical kinetics of a single microdischarge inside a forming gas bubble using 0-D-plasma chemical kinetics simulations. In place of a fully self-consistent approach, microdischarge properties, including bubble size and power deposition, are taken from experimental measurements carried out on a system specialised for the characterisation of single microdischarges. These properties are used as an input to the 0-D simulations, which consider the gas-phase chemical kinetics during the gas bubble lifetime. The goal is a better understanding of the processes inside the bubble and the possibility of controlling the plasma parameters to create a coating with predefined properties.

2. Experimental measurements: single microdischarge setup

The PEO process is generally characterised by transient microdischarges stochastically distributed across the surface of the electrode. To simplify these dynamics and study the development of individual microdischarges, a single microdischarge (SMD) setup has been developed [2]. The setup consists of an active anode, realised through an aluminium wire with a diameter of 1 mm and a stainless-steel cathode surrounded by distilled water mixed with an electrolyte, typically KOH. Due to the small area of the wire, the ignition of single microdischarges can be realised. Optical emission spectroscopy and high-speed imaging, coupled with synchronised voltage and current measurements, allow for time-resolved analysis of a single microdischarge. The spectroscopy results permit the calculation of electron density and electron temperature.

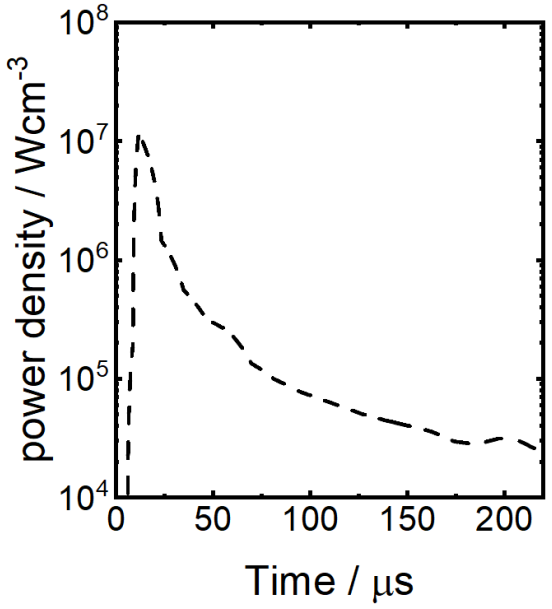

Fig. 1. Power per unit volume as a function of time, calculated from experimental measurements of current-voltage characteristics synchronised with bubble radius measurements. Conditions: Al anode, voltage ≈ 540 V, electrolyte, 1 g/l KOH, 10 minutes coating time.

The high-speed imaging of the microdischarge enables the determination of the bubble radius and, combined with the voltage-current measurements, the calculation of the power per unit volume, an example of which is shown in Fig. 1. The setup is described in more detail in the contribution of J.-L. Gembus *et al.*

3. Simulation method

A simplified sketch of a microdischarge within a gas bubble is shown in Fig. 2. The discharge forms on the electrode surrounded by the gas bubble, all contained in the electrolyte solution. To improve the understanding of the time evolution of the reactive species inside the gas bubble, the 0-D plasma-chemical kinetics code GlobalKin [3] is used. GlobalKin consists of three modules: a reaction chemistry and transport module, a two-term Boltzmann equation solver for calculating the electron energy distribution function (EEDF) and an ordinary differential equation (ODE) solver. The ODE solver allows for the time evolution of the charged and neutral species in the bubble to be calculated by solving the mass continuity equations for each species. In this work, only gas phase processes occurring within the lifetime of the bubble are considered. Interactions at solid surface and liquid interface are not considered, for the moment. The electron energy equation is also solved, considering the power input per unit volume and electron energy losses and gains from elastic and inelastic collisions.

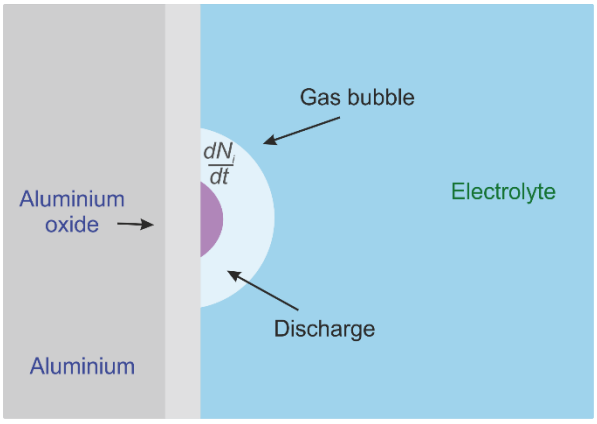

Fig. 2. Sketch of a microdischarge within a gas bubble on an aluminium electrode contained in an electrolyte solution.

For the simulations presented in this contribution, the gas temperature is assumed constant at 2000 K, based on estimates from the experimental setup. The pressure inside the bubble is set to 1 atm, also based on experimental measurements. The bubble is assumed to consist of pure water vapour at the start of microdischarge formation. The plasma-chemical reaction scheme used as input to the model is an adapted version of that published in [4, 5].

While this contribution focuses on simulations carried out using GlobalKin, progress on developing a new simulation framework designed explicitly for bubble-based microdischarges will also be discussed.

4. Results

Analysis of the experimentally measured current and voltage characteristics and bubble size as a function of time allows for power per unit volume associated with each microdischarge to be determined. This is shown in Fig. 1 for the case of an aluminium anode operated with a voltage of ≈ 540 V, an electrolyte consisting of 1 g/l KOH after a coating time of 10 minutes. Since the microdischarge current increases slightly earlier than the expansion of the bubble, there is a high power per unit volume early in the bubble lifetime, which then decreases significantly, with the bubble eventually collapsing after around 250 µs. Because of the high power per unit volume early in the microdischarge lifetime, the bubble properties appear to be largely defined in this time period. For example, the simulated electron density and temperature, using the power per unit volume profile shown in Fig. 1, are shown in Fig. 3. The electron density closely follows the power per unit volume, showing a large peak around 25 µs after the start of microdischarge formation, and much lower values for the remaining lifetime of the bubble and

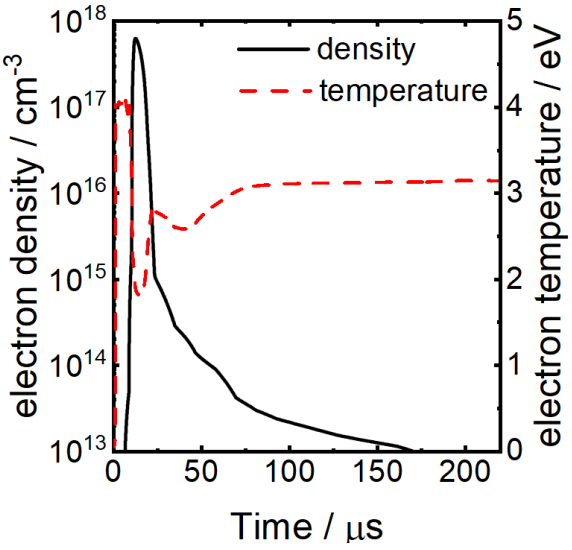

Fig. 3. Simulated electron density and electron temperature as a function of time for the power per unit volume profile shown in Fig. 1.

microdischarge. The electron temperature varies less as a function of time, reaching a minimum of around 2 eV during the region of high power deposition and staying around 3 eV for the rest of the bubble lifetime. In general, the electron properties are very sensitive to the peak power per unit volume. Because this occurs on short timescales at the start of bubble formation, it is difficult to fully resolve experimentally even with the high-speed diagnostics used. Therefore, the absolute values of power deposition and electron density are likely to be subject to large uncertainties. Improving the resolution in this region is an area of current work. However, it is generally clear that the large electron densities present during the initial phase of bubble formation lead to significant dissociation of the

water vapour inside the bubble and a highly complex variation of the reactive species densities as a function of time throughout the bubble lifetime. These and the associated plasma-chemical pathways towards ionisation and dissociation will be discussed in detail. In addition, current efforts to improve the model framework to achieve a more physically realistic representation of the complex spatial variations of plasma-produced species and the interaction with the solid surface and liquid electrolyte will be discussed.

5. Conclusion and Outlook

Preliminary simulation results using GlobalKin show a complex variation of the charged and neutral particle dynamics during microdischarge and bubble formation under typical PEO conditions. While the current model can provide general insights into these processes, it still represents a highly simplified treatment of the complex microdischarge dynamics. Efforts to improve the discharge model by introducing a more detailed treatment of the spatial inhomogeneity of the discharge will be presented.

6. Acknowledgement

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